PRINCIPLES OF MODERN CHEMISTRY

LibreTexts (Textmap of Oxtoby's Book)

Principles of Modern Chemistry

LibreTexts (Textmap of Oxtoby's Book)

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by Oxtoby, Gillis, and Campion

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Thumbnail: Spinning Buckminsterfullerene (C_{60}). (CC BY-SA 3.0; unported; Sponk).

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3: Chemical Bonding - The Classical Description

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7: Bonding in Organic Molecules

7.1: Petroleum Refining and the Hydrocarbons

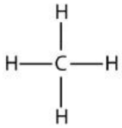
Learning Objectives

- To get an overview of hydrocarbons molecules and their four primary classifications

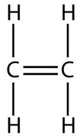
Hydrocarbons are organic compounds that contain **only** carbon and hydrogen. The four general classes of hydrocarbons are: alkanes, alkenes, alkynes and arenes. Aromatic compounds derive their names from the fact that many of these compounds in the early days of discovery were grouped because they were oils with fragrant odors.

The classifications for hydrocarbons, defined by IUPAC nomenclature of organic chemistry are as follows:

1. Saturated hydrocarbons (alkanes) are the simplest of the hydrocarbon species. They are composed entirely of single bonds and are saturated with hydrogen. The general formula for saturated hydrocarbons is C_nH_{2n+2} (assuming non-cyclic structures). Saturated hydrocarbons are the basis of petroleum fuels and are found as either linear or branched species.The simplest alkanes have their C atoms bonded in a straight chain; these are called *normal* alkanes. They are named according to the number of C atoms in the chain. The smallest alkane is methane:

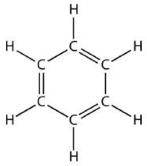


2. Unsaturated hydrocarbons have one or more double or triple bonds between carbon atoms. Those with double bond are called alkenes and those with one double bond have the formula C_nH_{2n} (assuming non-cyclic structures). Those containing triple bonds are called alkynes, with general formula C_nH_{2n-2}. The smallest alkene—ethene—has two C atoms and is also known by its common name ethylene:



The smallest alkyne is ethyne, which is also known as acetylene:

3. Cycloalkanes are hydrocarbons containing one or more carbon rings to which hydrogen atoms are attached. The general formula for a saturated hydrocarbon containing one ring is C_nH_{2n}.
4. Aromatic hydrocarbons, also known as arenes, are hydrocarbons that have at least one aromatic ring. Aromatic compounds contain the benzene unit. Benzene itself is composed of six C atoms in a ring, with alternating single and double C–C bonds:



Because of differences in molecular structure, the empirical formula remains different between hydrocarbons; in linear, or "straight-run" alkanes, alkenes and alkynes, the amount of bonded hydrogen lessens in alkenes and alkynes due to the "self-bonding" or catenation of carbon preventing entire saturation of the hydrocarbon by the formation of double or triple bonds.

The inherent ability of hydrocarbons to bond to themselves is known as catenation, and allows hydrocarbon to form more complex molecules, such as cyclohexane, and in rarer cases, arenes such as benzene. This ability comes from the fact that the bond character between carbon atoms is entirely non-polar, in that the distribution of electrons between the two elements is somewhat even due to the same electronegativity values of the elements (~0.30).

7.2: The Alkanes

Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in the molecules.

> The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

We previously introduced the three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) and they are shown again in Figure 7.2.1.

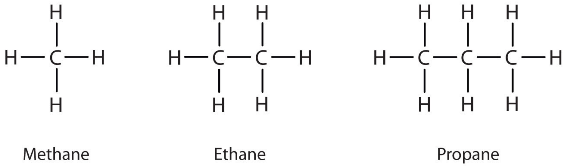


Figure 7.2.1: The Three Simplest Alkanes

The flat representations shown do not accurately portray bond angles or molecular geometry. Methane has a tetrahedral shape that chemists often portray with wedges indicating bonds coming out toward you and dashed lines indicating bonds that go back away from you. An ordinary solid line indicates a bond in the plane of the page. Recall that the VSEPR theory correctly predicts a tetrahedral shape for the methane molecule (Figure 7.2.2).

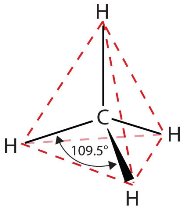


Figure 7.2.2: The Tetrahedral Methane Molecule

Methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH_2 unit. The first 10 members of this series are given in Table 7.2.1.

Table 7.2.1: The First 10 Straight-Chain Alkanes

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
methane	CH_4	CH_4	—
ethane	C_2H_6	CH_3CH_3	—
propane	C_3H_8	$CH_3CH_2CH_3$	—
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	3

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

Consider the series in Figure 7.2.3. The sequence starts with C_3H_8, and a CH_2 unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a CH_2 group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

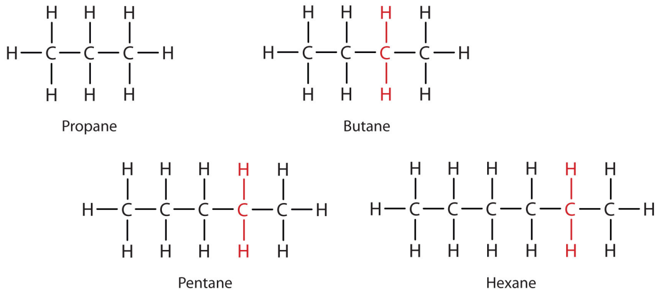


Figure 7.2.3: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

The principle of homology allows us to write a general formula for alkanes: C_nH_{2n+2}. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2 \times 8)+2} = C_8H_{18}$.

Key Takeaway

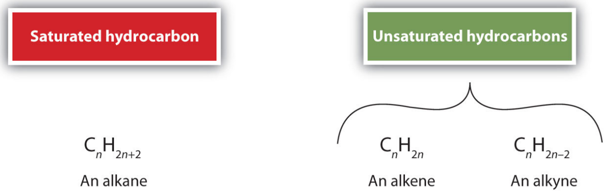
- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.

7.3: The Alkenes and Alkynes

Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C{=}CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds ($R{-}C{\equiv}C{-}R$). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

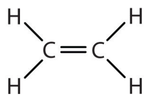


Some representative alkenes—their names, structures, and physical properties—are given in Table 7.3.1.

Table 7.3.1: Physical Properties of Some Selected Alkenes

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
ethene	C_2H_4	$CH_2{=}CH_2$	–169	–104
propene	C_3H_6	$CH_2{=}CHCH_3$	–185	–47
1-butene	C_4H_8	$CH_2{=}CHCH_2CH_3$	–185	–6
1-pentene	C_5H_{10}	$CH_2{=}CH(CH_2)_2CH_3$	–138	30
1-hexene	C_6H_{12}	$CH_2{=}CH(CH_2)_3CH_3$	–140	63
1-heptene	C_7H_{14}	$CH_2{=}CH(CH_2)_4CH_3$	–119	94
1-octene	C_8H_{16}	$CH_2{=}CH(CH_2)_5CH_3$	–102	121

We used only condensed structural formulas in Table 7.3.1. Thus, $CH_2{=}CH_2$ stands for



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is C_2H_4, whereas that for ethane is C_2H_6.

The first two alkenes in Table 7.3.1, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure 7.3.1). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.

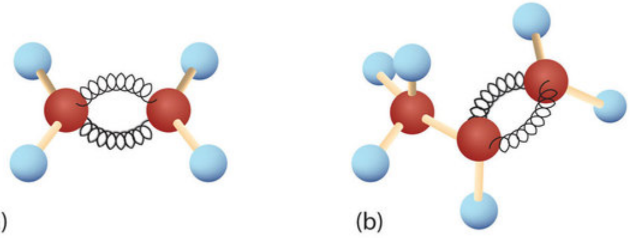
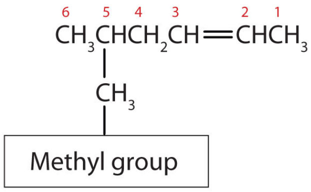


Figure 7.3.1: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

> Although there is only one alkene with the formula C_2H_4 (ethene) and only one with the formula C_3H_6 (propene), there are several alkenes with the formula C_4H_8.

Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound $CH_2{=}CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers.The compound $CH_3CH{=}CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*

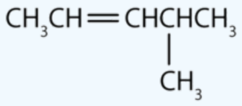


$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH{=}CHCH_3$

Example 7.3.1

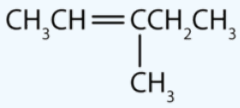
Name each compound.

a.



$CH_3CH{=}CH\underset{\underset{CH_3}{|}}{C}HCH_3$

b.



$CH_3CH{=}\underset{\underset{CH_3}{|}}{C}CH_2CH_3$

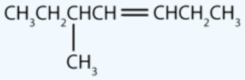
Solution

a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.
b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

Exercise 7.3.1

Name each compound.

a. $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$

b. 

$$\begin{array}{l} CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH{=}CHCH_2CH_3 \end{array}$$

Answer

Just as there are cycloalkanes, there are *cycloalkenes*. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name.

Example 7.3.2

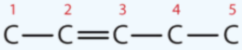
Draw the structure for each compound.

a. 3-methyl-2-pentene
b. cyclohexene

Solution

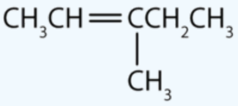
a.

First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:



$$C{-}C{=}C{-}C{-}C$$

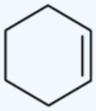
Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



$$CH_3CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CH_2CH_3$$

b

First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and -*ene* means a double bond.



Exercise 7.3.2

Draw the structure for each compound.

a. 2-ethyl-1-hexene
b. cyclopentene

Key Takeaway

- Alkenes are hydrocarbons with a carbon-to-carbon double bond.

- **13.1: Alkenes- Structures and Names** by Anonymous is licensed CC BY-NC-SA 3.0. Original source: https://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological.

7.4: Aromatic Hydrocarbons

Learning Objectives

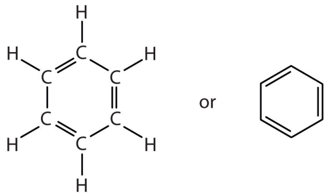
- To describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes.

Next we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties. We start with the simplest of these compounds. Benzene (C_6H_6) is of great commercial importance, but it also has noteworthy health effects.

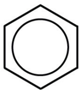
The formula C_6H_6 seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula C_6H_{14}—eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

> Benzene is a liquid that smells like gasoline, boils at 80°C, and freezes at 5.5°C. It is the aromatic hydrocarbon produced in the largest volume. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.

To explain the surprising properties of benzene, chemists suppose the molecule has a cyclic, hexagonal, planar structure of six carbon atoms with one hydrogen atom bonded to each. We can write a structure with alternate single and double bonds, either as a full structural formula or as a line-angle formula:



However, these structures do not explain the unique properties of benzene. Furthermore, experimental evidence indicates that all the carbon-to-carbon bonds in benzene are equivalent, and the molecule is unusually stable. Chemists often represent benzene as a hexagon with an inscribed circle:



The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are *delocalized*, or spread out, over all the carbon atoms). It is understood that each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it. Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon. We use this modern symbolism, but many scientists still use the earlier structure with alternate double and single bonds.

To Your Health: Benzene and Us

Most of the benzene used commercially comes from petroleum. It is employed as a starting material for the production of detergents, drugs, dyes, insecticides, and plastics. Once widely used as an organic solvent, benzene is now known to have both short- and long-term toxic effects. The inhalation of large concentrations can cause nausea and even death due to respiratory or

> heart failure, while repeated exposure leads to a progressive disease in which the ability of the bone marrow to make new blood cells is eventually destroyed. This results in a condition called *aplastic anemia*, in which there is a decrease in the numbers of both the red and white blood cells.

Key Takeaway

- Aromatic hydrocarbons appear to be unsaturated, but they have a special type of bonding and do not undergo addition reactions.

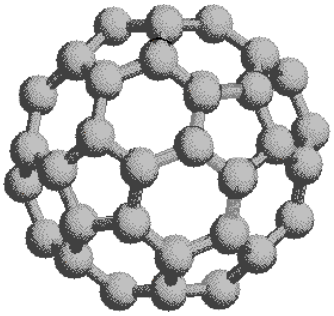
7.5: Fullerenes

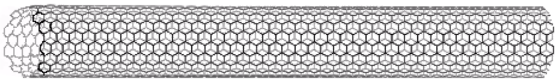
If we extend the structure of corannulene by adding similar cycles of five benzene rings, the curvature of the resulting molecule should increase, and eventually close into a sphere of carbon atoms. The archetypical compound of this kind (C_{60}) has been named **buckminsterfullerene** because of its resemblance to the geodesic structures created by Buckminster Fuller. It is a member of a family of similar carbon structures that are called **fullerenes**. These materials represent a third class of carbon allotropes. Alternating views of the C_{60} fullerene structure are shown on the right, together with a soccer ball-like representation of the 12 five and 20 six-membered rings composing its surface. Precise measurement by Atomic Force Microscopy (AFM) has shown that the C-C bond lengths of the six-membered rings are not all equal, and depend on whether the ring is fused to a five or six-membered beighbor. By clicking on this graphic, a model of C_{60} will be displayed.

Although C_{60} is composed of fused benzene rings its chemical reactivity resembles that of the cycloalkenes more than benzene. Indeed, exposure to light and oxygen slowly degrade fullerenes to cage opened products. Most of the reactions thus far reported for C_{60} involve addition to, rather than substitution of, the core structure. These reactions include hydrogenation, bromination and hydroxylation. Strain introduced by the curvature of the surface may be responsible for the enhanced reactivity of C_{60}.

. Larger fullerenes, such as C_{70}, C_{76}, C_{82} & C_{84}have ellipsoidal or distorted spherical structures, and fullerene-like assemblies up to C_{240} have been detected. A fascinating aspect of these structures is that the space within the carbon cage may hold atoms, ions or small molecules. Such species are called **endohedral fullerenes**. The cavity of C_{60} is relatively small, but encapsulated helium, lithium and atomic nitrogen compounds have been observed. Larger fullerenes are found to encapsulate lanthanide metal atoms.

Interest in the fullerenes has led to the discovery of a related group of carbon structures referred to as nanotubes. As shown in the following illustration, nanotubes may be viewed as rolled up segments of graphite. The chief structural components are six-membered rings, but changes in tube diameter, branching into side tubes and the capping of tube ends is accomplished by fusion with five and seven-membered rings. Many interesting applications of these unusual structures have been proposed.



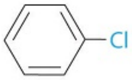
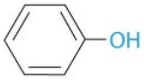
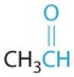
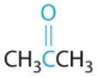
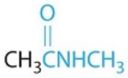
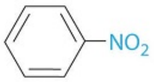


7.6: Functional Groups and Organic Reactions

Learning Objectives

- To know the major classes of organic compounds and identify important functional groups.

You were previously introduced to several structural units that chemists use to classify organic compounds and predict their reactivities. These functional groups, which determine the chemical reactivity of a molecule under a given set of conditions, can consist of a single atom (such as Cl) or a group of atoms (such as CO_2H). The major families of organic compounds are characterized by their functional groups. Figure $7.6.1$ summarizes five families introduced in earlier chapters, gives examples of compounds that contain each functional group, and lists the suffix or prefix used in the systematic nomenclature of compounds that contain each functional group.

Class	**General Formula**	**Example**	**Common Name (Systematic Name)**	**Common Suffix/Prefix (Systematic)**
		Hydrocarbons		
Alkanes	RH	CH_3CH_3	ethane	-ane
Alkenes	$RR'C{=}CR''R'''$	$H_2C{=}CH_2$	ethylene (ethene)	-ene
Alkynes	$RC{\equiv}CR'$	$HC{\equiv}CH$	acetylene (ethyne)	(-yne)
Arenes	ArH[a]		benzene	-ene
		Halogen-Containing Compounds		
Alkyl halides	RX	CH_3CH_2Cl	ethyl chloride (chloroethane)	halide (halo-)
Aryl halides	ArX[a]		chlorobenzene	halo-
		Oxygen-Containing Compounds		
Alcohols	ROH[a]	CH_3CH_2OH	ethyl alcohol (ethanol)	-ol
Phenols	ArOH[b]		phenol	-ol
Ethers	ROR′	$H_3CH_2COCH_2CH_3$	diethyl ether	ether
Aldehydes	RCHO	 $CH_3\overset{O}{\overset{\|}{C}}H$	acetaldehyde (ethanal)	-aldehyde (-al)
Ketones	$RR'C{=}O$	 $CH_3\overset{O}{\overset{\|}{C}}CH_3$	acetone (2-propanone)	-one
Carboxylic acids	RCO_2H	 $CH_3\overset{O}{\overset{\|}{C}}OH$	acetic acid (ethanoic acid)	-ic acid (-oic acid)
		Carboxylic Acid Derivatives		
Esters	RCO_2R'	 $CH_3\overset{O}{\overset{\|}{C}}OCH_3$	methyl acetate (methyl ethanoate)	-ate (-oate)
Amides	RCONHR′	 $CH_3\overset{O}{\overset{\|}{C}}NHCH_3$	*N*-methylacetamide	-amide
		Nitrogen-Containing Compounds		
Amines	RNH_2, RNHR′, RNR′R″	$CH_3CH_2NH_2$	ethylamine	-amine
Nitriles	$RC{\equiv}N$	$H_3CC{\equiv}N$	acetonitrile	-nitrile
Nitro compounds	$ArNO_2$[a]		nitrobenzene	nitro-

[a]R indicates an alkyl group [b]Ar indicates an *aryl* group.

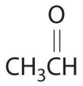
Figure 7.6.1: Major Classes of Organic Compounds

The first family listed in Figure 7.6.1 is the hydrocarbons. These include alkanes, with the general molecular formula C_nH_{2n+2} where n is an integer; alkenes, represented by C_nH_{2n}; alkynes, represented by C_nH_{2n-2}; and arenes. Halogen-substituted alkanes, alkenes, and arenes form a second major family of organic compounds, which include the alkyl halides and the aryl halides. Oxygen-containing organic compounds, a third family, may be divided into two main types: those that contain at least one C–O bond, which include alcohols, phenols (derivatives of benzene), and ethers, and those that contain a carbonyl group (C=O), which include aldehydes, ketones, and carboxylic acids. Carboxylic acid derivatives, the fourth family listed, are compounds in which the OH of the $–CO_2H$ functional group is replaced by either an alkoxy (–OR) group, producing an ester, or by an amido (–NRR′, where R and R′ can be H and/or alkyl groups), forming an amide. Nitrogen-containing organic compounds, the fifth family, include amines; nitriles, which have a C≡N bond; and nitro compounds, which contain the $–NO_2$ group.

The systematic nomenclature of organic compounds indicates the positions of substituents using the lowest numbers possible to identify their locations in the carbon chain of the parent compound. If two compounds have the same systematic name, then they are the same compound. Although systematic names are preferred because they are unambiguous, many organic compounds are known by their common names rather than their systematic names. Common nomenclature uses the prefix form—for a compound that contains no carbons other than those in the functional group, and acet—for those that have one carbon atom in addition [two in the case of acetone, $(CH_3)_2C=O$]. Thus methanal and ethanal, respectively, are the systematic names for formaldehyde and acetaldehyde.

$\overset{\displaystyle O}{\overset{\|}{\text{HCH}}}$

Formaldehyde
(methanal)



$CH_3\overset{\displaystyle O}{\overset{\|}{\text{C}}}H$

Acetaldehyde
(ethanal)

Recall that in the systematic nomenclature of aromatic compounds, the positions of groups attached to the aromatic ring are indicated by numbers, starting with 1 and proceeding around the ring in the direction that produces the lowest possible numbers. For example, the position of the first CH_3 group in dimethyl benzene is indicated with a 1, but the second CH_3 group, which can be placed in any one of three positions, produces 1,2-dimethylbenzene, 1,3-dimethylbenzene, or 1,4-dimethylbenzene (Figure 7.6.2). In common nomenclature, in contrast, the prefixes ortho-, meta-, and para- are used to describe the relative positions of groups attached to an aromatic ring. If the CH_3 groups in dimethylbenzene, whose common name is xylene, are adjacent to each other, the compound is commonly called ortho-xylene, abbreviated o-xylene. If they are across from each other on the ring, the compound is commonly called para-xylene or p-xylene. When the arrangement is intermediate between those of ortho- and para- compounds, the name is meta-xylene or m-xylene.

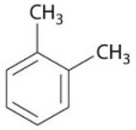
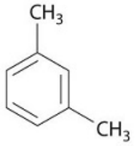
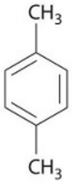
Prefix	Positions of Methyl Groups	Example	Common Name (Systematic Name)
ortho-	1,2		*o*-xylene (1,2-dimethylbenzene)
meta-	1,3		*m*-xylene (1,3-dimethylbenzene)
para-	1,4		*p*-xylene (1,4-dimethylbenzene)

Figure 7.6.2: Common Nomenclature for Aromatic Ring Substitutions

We begin our discussion of the structure and reactivity of organic compounds by exploring structural variations in the simple saturated hydrocarbons known as alkanes. These compounds serve as the scaffolding to which the various functional groups are most often attached.

Summary

Functional groups determine the chemical reactivity of an organic molecule. Functional groups are structural units that determine the chemical reactivity of a molecule under a given set of conditions. Organic compounds are classified into several major categories based on the functional groups they contain. In the systematic names of organic compounds, numbers indicate the positions of functional groups in the basic hydrocarbon framework. Many organic compounds also have common names, which use the prefix form—for a compound that contains no carbons other than those in the functional group and acet—for those that have one additional carbon atom.

Conceptual Problems

1. Can two substances have the same systematic name and be different compounds?
2. Is a carbon–carbon multiple bond considered a functional group?

7.7: Pesticides and Pharmaceuticals

CHAPTER OVERVIEW

8: Bonding in Transition Metal Compounds and Coordination Complexes

Topic hierarchy

8.1: Chemistry of the Transition Metals

This page explains what a transition metal is in terms of its electronic structure, and then goes on to look at the general features of transition metal chemistry. These include variable oxidation state (oxidation number), complex ion formation, colored ions, and catalytic activity.

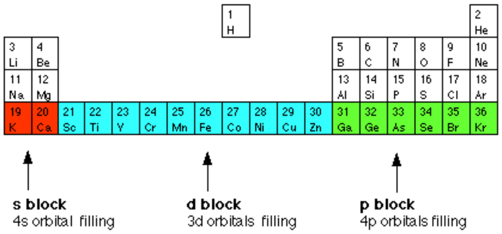
What is a transition metal?

The terms transition metal (or element) and d block element are sometimes used as if they mean the same thing. They don't - there's a subtle difference between the two terms. We'll explore d block elements first:

d-block elements

You will remember that when you are building the Periodic Table and working out where to put the electrons using the Aufbau Principle, something odd happens after argon.

At argon, the 3s and 3p levels are full, but rather than fill up the 3d levels next, the 4s level fills instead to give potassium and then calcium. Only after that do the 3d levels fill. The elements in the Periodic Table which correspond to the d levels filling are called **d block elements**. The first row of these is shown in the shortened form of the Periodic Table below.



The electronic structures of the d block elements shown are:

Sc	[Ar] $\mathbf{3d^{1}}4s^{2}$
Ti	[Ar] $\mathbf{3d^{2}}4s^{2}$
V	[Ar] $\mathbf{3d^{3}}4s^{2}$
Cr	[Ar] $\mathbf{3d^{5}4s^{1}}$
Mn	[Ar] $\mathbf{3d^{5}4s^{2}}$
Fe	[Ar] $\mathbf{3d^{6}}4s^{2}$
Co	[Ar] $\mathbf{3d^{7}}4s^{2}$
Ni	[Ar] $\mathbf{3d^{8}}4s^{2}$
Cu	[Ar] $\mathbf{3d^{10}4s^{1}}$
Zn	[Ar] $\mathbf{3d^{10}4s^{2}}$

You will notice that the pattern of filling is not entirely tidy! It is broken at both chromium and copper.

Transition metals

> Not all d block elements count as transition metals! There are two slightly different definitions in use at the moment both of which crop up in various uses:
>
> *The official IUPAC definition:*
>
> **A transition metal is one which has an atom with an incompletely filled d orbital or which forms one or more stable ions with incompletely filled d orbitals.**
>
> *The older definition:*

> **A transition metal is one which forms one or more stable ions which have *incompletely* filled d orbitals.**

Notice how similar these two definitions are. The only difference is that the IUPAC definition allows for the atom itself having incompletely filled d levels as well as the ions.

The problem lies only at the extreme left-hand end of the d block with, for example, scandium: Scandium has the electronic structure [Ar] $3d^1 4s^2$. When it forms ions, it always loses the 3 outer electrons and ends up with an argon structure. The Sc^{3+} ion has **no d electrons** and so does not meet the second (older) definition.

Zinc has the electronic structure [Ar] $3d^{10} 4s^2$. When it forms ions, it always loses the two 4s electrons to give a 2+ ion with the electronic structure [Ar] $3d^{10}$. The zinc ion has **full d levels** and does not meet either definition.

By contrast, copper, [Ar] $3d^{10} 4s^1$, forms two ions. In the Cu^+ ion the electronic structure is [Ar] $3d^{10}$. However, the more common Cu^{2+} ion has the structure [Ar] $3d^9$. Copper is definitely a transition metal because the Cu^{2+} ion has an incomplete d level.

Transition metal ions

Here you are faced with one of the most irritating facts in chemistry at this level! When you work out the electronic structures of the first transition series (from scandium to zinc) using the Aufbau Principle, you do it on the basis that the 3d orbitals have higher energies than the 4s orbitals.

That means that you work on the assumption that the 3d electrons are added after the 4s ones. However, in all the chemistry of the transition elements, the 4s orbital behaves as the outermost, highest energy orbital.

> It is important to note that when d block elements form ions, the 4s electrons are always lost first.

To write the electronic structure for Co^{2+}:

Co		[Ar] $3d^7 4s^2$
Co^{2+}		[Ar] $3d^7$

The 2+ ion is formed by the loss of the two 4s electrons.

To write the electronic structure for V^{3+}:

V		[Ar] $3d^3 4s^2$
V^{3+}		[Ar] $3d^2$

The 4s electrons are lost first followed by one of the 3d electrons.

Variable oxidation state (number)

One of the key features of transition metal chemistry is the wide range of oxidation states (oxidation numbers) that the metals can show. It would be wrong, though, to give the impression that only transition metals can have variable oxidation states. For example, elements like Sulfur or nitrogen or chlorine have a very wide range of oxidation states in their compounds - and these obviously aren't transition metals. However, this variability is less common in metals apart from the transition elements. Of the familiar metals from the main groups of the Periodic Table, only lead and tin show variable oxidation state to any extent.

Examples of variable oxidation states in the transition metals

- **Iron:** Iron has two common oxidation states (+2 and +3) in, for example, Fe^{2+} and Fe^{3+}. It also has a less common +6 oxidation state in the ferrate(VI) ion, FeO_4^{2-}.
- **Manganese:** Manganese has a very wide range of oxidation states in its compounds. For example:

+2	in Mn^{2+}

+3	in Mn_2O_3
+4	in MnO_2
+6	in MnO_4^{2-}
+7	in MnO_4^-

You will find the above examples and others looked at in detail if you explore the chemistry of individual metals from the transition metal menu. There is a link to this menu at the bottom of the page.

Explaining the variable oxidation states in the transition metals

We'll look at the formation of simple ions like Fe^{2+} and Fe^{3+}. When a metal forms an ionic compound, the formula of the compound produced depends on the energetics of the process. On the whole, the compound formed is the one in which most energy is released. The more energy released, the more stable the compound. There are several energy terms to think about, but the key ones are:

- The amount of energy needed to ionize the metal (the sum of the various ionization energies)
- The amount of energy released when the compound forms. This will either be lattice enthalpy if you are thinking about solids, or the hydration enthalpies of the ions if you are thinking about solutions.

The more highly charged the ion, the more electrons you have to remove and the more ionization energy you will have to provide. But off-setting this, the more highly charged the ion, the more energy is released either as lattice enthalpy or the hydration enthalpy of the metal ion.

Thinking about a typical non-transition metal (calcium)

The formula for Calcium chloride is $CaCl_2$. Why is that? If you tried to make CaCl, (containing a Ca^+ ion), the overall process is slightly exothermic. By making a Ca^{2+} ion instead, you have to supply more ionization energy, but you get out lots more lattice energy. There is much more attraction between chloride ions and Ca^{2+} ions than there is if you only have a 1+ ion. The overall process is very exothermic. Because the formation of $CaCl_2$ releases much more energy than making CaCl, then $CaCl_2$ is more stable - and so forms instead.

What about $CaCl_3$? This time you have to remove yet another electron from calcium. The first two come from the 4s level. The third one comes from the 3p. That is much closer to the nucleus and therefore much more difficult to remove. There is a large jump in ionization energy between the second and third electron removed. Although there will be a gain in lattice enthalpy, it is not anything like enough to compensate for the extra ionization energy, and the overall process is very endothermic. It definitely is not energetically sensible to make $CaCl_3$!

Thinking about a typical transition metal (iron)

Here are the changes in the electronic structure of iron to make the 2+ or the 3+ ion.

Fe		[Ar] $3d^64s^2$
Fe^{2+}		[Ar] $3d^6$
Fe^{3+}		[Ar] $3d^5$

The 4s orbital and the 3d orbitals have very similar energies. There is not a huge jump in the amount of energy you need to remove the third electron compared with the first and second. The figures for the first three ionization energies (in kJ mol^{-1}) for iron compared with those of calcium are:

metal	1st IE	2nd IE	3rd IE
Ca	590	1150	4940
Fe	762	1560	2960

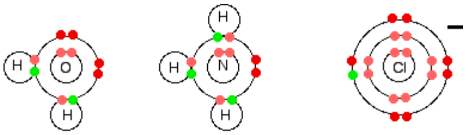
There is an increase in ionization energy as you take more electrons off an atom because you have the same number of protons attracting fewer electrons. However, there is much less increase when you take the third electron from iron than from calcium.

In the iron case, the extra ionization energy is compensated more or less by the extra lattice enthalpy or hydration enthalpy evolved when the 3+ compound is made. The net effect of all this is that the overall enthalpy change is not vastly different whether you make, say, $FeCl_2$ or $FeCl_3$. That means that it is not too difficult to convert between the two compounds.

The formation of complex ions

What is a complex ion?

A complex ion has a metal ion at its center with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by coordinate (dative covalent) bonds (in some cases, the bonding is actually more complicated). The molecules or ions surrounding the central metal ion are called ligands. Simple ligands include water, ammonia and chloride ions.



What all these have got in common is active lone pairs of electrons in the outer energy level. These are used to form co-ordinate bonds with the metal ion.

Some examples of complex ions formed by transition metals

$[Fe(H_2O)_6]^{2+}$

$[Co(NH_3)_6]^{2+}$

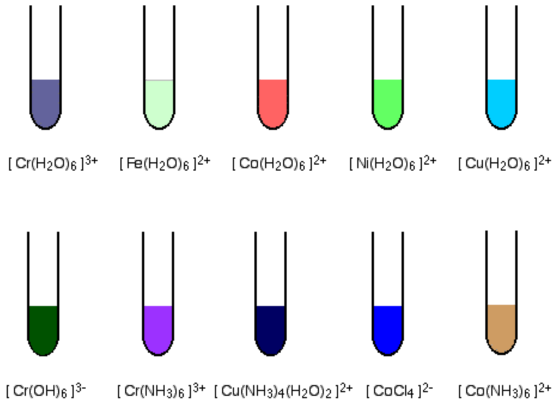
$[Cr(OH)_6]^{3-}$

$[CuCl_4]^{2-}$

Other metals also form complex ions - it is not something that only transition metals do. Transition metals do, however, form a very wide range of complex ions.

The formation of colored compounds

The diagrams show approximate colors for some common transition metal complex ions.



You will find these and others discussed if you follow links to individual metals from the transition metal menu (link at the bottom of the page). Alternatively, you could explore the complex ions menu (follow the link in the help box which has just disappeared off the top of the screen).

The origin of color in the transition metal ions

When white light passes through a solution of one of these ions, or is reflected off it, some colors in the light are absorbed. The color you see is how your eye perceives what is left. Attaching ligands to a metal ion has an effect on the energies of the d orbitals.

Light is absorbed as electrons move between one d orbital and another. This is explained in detail on another page.

Catalytic Activity

Transition metals and their compounds are often good catalysts. A few of the more obvious cases are mentioned below, but you will find catalysis explored in detail elsewhere on the site (follow the link after the examples). Transition metals and their compounds function as catalysts either because of their ability to change oxidation state or, in the case of the metals, to adsorb other substances on to their surface and activate them in the process. All this is explored in the main catalysis section.

Iron in the Haber Process

The Haber Process combines hydrogen and nitrogen to make ammonia using an iron catalyst.

$$N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{Fe} 2NH_{3(g)}$$

Nickel in the hydrogenation of C=C bonds

This reaction is at the heart of the manufacture of margarine from vegetable oils. However, the simplest example is the reaction between ethene and hydrogen in the presence of a nickel catalyst.

$$CH_2{=}CH_2 + H_2 \xrightarrow{Ni} CH_3CH_3$$

Transition metal compounds as catalysts

Vanadium(V) oxide in the Contact Process

At the heart of the Contact Process is a reaction which converts Sulfur dioxide into Sulfur trioxide. Sulfur dioxide gas is passed together with air (as a source of oxygen) over a solid vanadium(V) oxide catalyst.

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{V_2O_5} 2SO_{3(g)}$$

Iron ions in the reaction between persulfate ions and iodide ions

Persulphate ions (peroxodisulphate ions), $S_2O_8^{2-}$, are very powerful oxidizing agents. Iodide ions are very easily oxidized to iodine. And yet the reaction between them in solution in water is very slow. The reaction is catalyzed by the presence of either iron(II) or iron(III) ions.

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

Contributors and Attributions

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8.2: Bonding in Simple Molecules That Contain Transition Metals

The oxidation state of an element is related to the number of electrons that an atom loses, gains, or appears to use when joining with another atom in compounds. It also determines the ability of an atom to oxidize (to lose electrons) or to reduce (to gain electrons) other atoms or species. Almost all of the transition metals have multiple oxidation states experimentally observed.

Introduction

Filling atomic orbitals requires a set number of electrons. The s-block is composed of elements of Groups I and II, the alkali and alkaline earth metals (sodium and calcium belong to this block). Groups XIII through XVIII comprise of the p-block, which contains the nonmetals, halogens, and noble gases (carbon, nitrogen, oxygen, fluorine, and chlorine are common members). Transition metals reside in the d-block, between Groups III and XII. If the following table appears strange, or if the orientations are unclear, please review the section on atomic orbitals.

Table 8.2.1

s Orbital	p Orbitals	d Orbitals
1 orbital, 2 electrons	3 orbitals: p_x, p_y, p_z; 6 electrons	5 orbitals: $d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{yz}, d_{xz}; 10 electrons
	Highest energy orbital for a given quantum number n	Degenerate with s-orbital of quantum number n+1

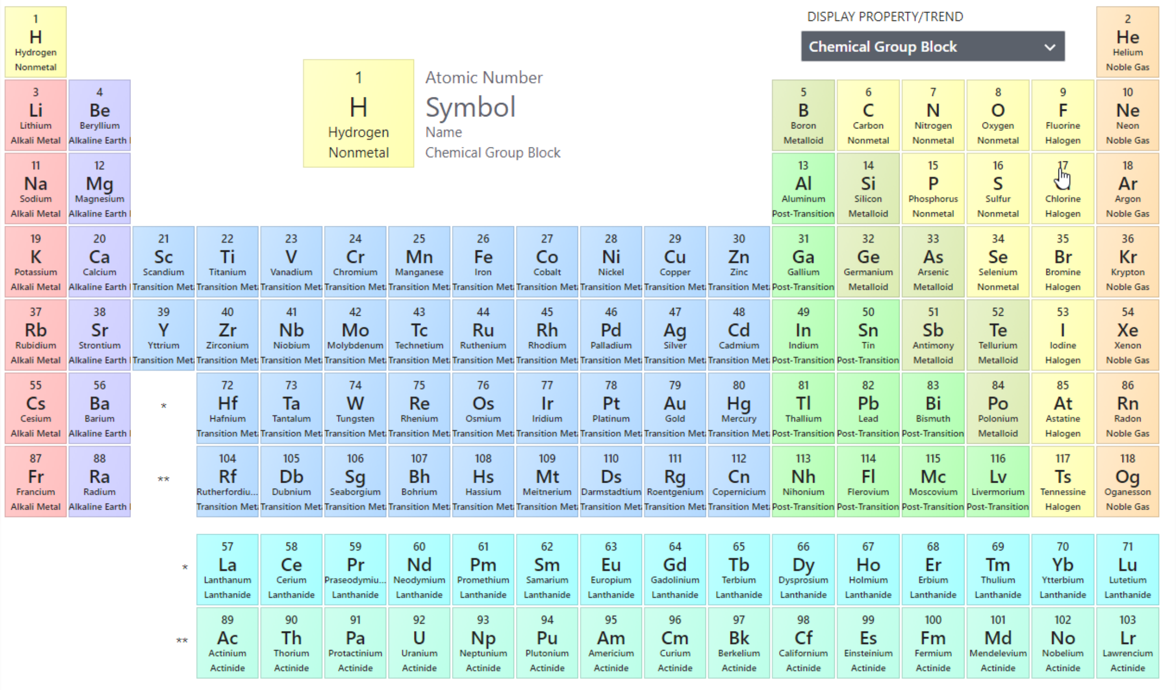
The key thing to remember about electronic configuration is that the most stable noble gas configuration is ideal for any atom. Forming bonds are a way to approach that configuration. In particular, the transition metals form more lenient bonds with anions, cations, and neutral complexes in comparison to other elements. This is because the d orbital is rather diffused (the f orbital of the lanthanide and actinide series more so).

Neutral-Atom Electron Configurations

Counting through the periodic table is an easy way to determine which electrons exist in which orbitals. As mentioned before, by counting protons (atomic number), you can tell the number of electrons in a neutral atom. Organizing by block quickens this process. For example, if we were interested in determining the electronic organization of **Vanadium** (atomic number 23), we would start from hydrogen and make our way down the the Periodic Table).

1s (H, He), 2s (Li, Be), 2p (B, C, N, O, F, Ne), 3s (Na, Mg), 3p (Al, Si, P, S, Cl, Ar), 4s (K, Ca), 3d (Sc, Ti, V).

If you do not feel confident about this counting system and how electron orbitals are filled, please see the section on electron configuration.



1 H Hydrogen Nonmetal																	2 He Helium Noble Gas
3 Li Lithium Alkali Metal	4 Be Beryllium Alkaline Earth											5 B Boron Metalloid	6 C Carbon Nonmetal	7 N Nitrogen Nonmetal	8 O Oxygen Nonmetal	9 F Fluorine Halogen	10 Ne Neon Noble Gas
11 Na Sodium Alkali Metal	12 Mg Magnesium Alkaline Earth											13 Al Aluminum Post-Transition	14 Si Silicon Metalloid	15 P Phosphorus Nonmetal	16 S Sulfur Nonmetal	17 Cl Chlorine Halogen	18 Ar Argon Noble Gas
19 K Potassium Alkali Metal	20 Ca Calcium Alkaline Earth	21 Sc Scandium Transition Met	22 Ti Titanium Transition Met	23 V Vanadium Transition Met	24 Cr Chromium Transition Met	25 Mn Manganese Transition Met	26 Fe Iron Transition Met	27 Co Cobalt Transition Met	28 Ni Nickel Transition Met	29 Cu Copper Transition Met	30 Zn Zinc Transition Met	31 Ga Gallium Post-Transition	32 Ge Germanium Metalloid	33 As Arsenic Metalloid	34 Se Selenium Nonmetal	35 Br Bromine Halogen	36 Kr Krypton Noble Gas
37 Rb Rubidium Alkali Metal	38 Sr Strontium Alkaline Earth	39 Y Yttrium Transition Met	40 Zr Zirconium Transition Met	41 Nb Niobium Transition Met	42 Mo Molybdenum Transition Met	43 Tc Technetium Transition Met	44 Ru Ruthenium Transition Met	45 Rh Rhodium Transition Met	46 Pd Palladium Transition Met	47 Ag Silver Transition Met	48 Cd Cadmium Transition Met	49 In Indium Post-Transition	50 Sn Tin Post-Transition	51 Sb Antimony Metalloid	52 Te Tellurium Metalloid	53 I Iodine Halogen	54 Xe Xenon Noble Gas
55 Cs Cesium Alkali Metal	56 Ba Barium Alkaline Earth	*	72 Hf Hafnium Transition Met	73 Ta Tantalum Transition Met	74 W Tungsten Transition Met	75 Re Rhenium Transition Met	76 Os Osmium Transition Met	77 Ir Iridium Transition Met	78 Pt Platinum Transition Met	79 Au Gold Transition Met	80 Hg Mercury Transition Met	81 Tl Thallium Post-Transition	82 Pb Lead Post-Transition	83 Bi Bismuth Post-Transition	84 Po Polonium Metalloid	85 At Astatine Halogen	86 Rn Radon Noble Gas
87 Fr Francium Alkali Metal	88 Ra Radium Alkaline Earth	**	104 Rf Rutherfordiu... Transition Met	105 Db Dubnium Transition Met	106 Sg Seaborgium Transition Met	107 Bh Bohrium Transition Met	108 Hs Hassium Transition Met	109 Mt Meitnerium Transition Met	110 Ds Darmstadtium Transition Met	111 Rg Roentgenium Transition Met	112 Cn Copernicium Transition Met	113 Nh Nihonium Post-Transition	114 Fl Flerovium Post-Transition	115 Mc Moscovium Post-Transition	116 Lv Livermorium Post-Transition	117 Ts Tennessine Halogen	118 Og Oganesson Noble Gas
		*	57 La Lanthanum Lanthanide	58 Ce Cerium Lanthanide	59 Pr Praseodymiu... Lanthanide	60 Nd Neodymium Lanthanide	61 Pm Promethium Lanthanide	62 Sm Samarium Lanthanide	63 Eu Europium Lanthanide	64 Gd Gadolinium Lanthanide	65 Tb Terbium Lanthanide	66 Dy Dysprosium Lanthanide	67 Ho Holmium Lanthanide	68 Er Erbium Lanthanide	69 Tm Thulium Lanthanide	70 Yb Ytterbium Lanthanide	71 Lu Lutetium Lanthanide
		**	89 Ac Actinium Actinide	90 Th Thorium Actinide	91 Pa Protactinium Actinide	92 U Uranium Actinide	93 Np Neptunium Actinide	94 Pu Plutonium Actinide	95 Am Americium Actinide	96 Cm Curium Actinide	97 Bk Berkelium Actinide	98 Cf Californium Actinide	99 Es Einsteinium Actinide	100 Fm Fermium Actinide	101 Md Mendelevium Actinide	102 No Nobelium Actinide	103 Lr Lawrencium Actinide

Figure 8.2.1: Periodic Table (Public Domain; PubChem)

Referring to the periodic table below confirms this organization. We have three elements in the 3d orbital. Therefore, we write in the order the orbitals were filled.

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$$

or

$$[Ar]\ 4s^2\ 3d^3.$$

The neutral atom configurations of the fourth period transition metals are in Table 8.2.2.

Table 8.2.2

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
[Ar] $4s^23d^1$	[Ar] $4s^23d^2$	[Ar] $4s^23d^3$	[Ar] ~~$4s^23d^4$~~	[Ar] $4s^23d^5$	[Ar] $4s^23d^6$	[Ar] $4s^23d^7$	[Ar] $4s^23d^8$	[Ar] ~~$4s^23d^9$~~	[Ar] $4s^23d^{10}$
			[Ar] $4s^13d^5$					[Ar] $4s^13d^{10}$	

Chromium and copper appear anomalous. Take a brief look at where the element **Chromium** (atomic number 24) lies on the Periodic Table (Figure 8.2.1). The electronic configuration for chromium is not [Ar] $4s^23d^4$ but instead it is [Ar] $4s^13d^5$. This is because the half-filled 3d manifold (with one 4s electron) is more stable than a partially filled d-manifold (and a filled 4s manifold). You will notice from Table 8.2.2 that the copper exhibits a similar phenomenon, although with a fully filled d-manifold.

Oxidation States of Transition Metal Ions

When considering ions, we add or subtract negative charges from an atom. Keeping the atomic orbitals when assigning oxidation numbers in mind helps in recognizing that transition metals pose a special case, but not an exception to this convenient method. An atom that accepts an electron to achieve a more stable configuration is assigned an oxidation number of -1. The donation of an electron is then +1. When a transition metal loses electrons, it tends to lose it's s orbital electrons before any of its d orbital electrons. For more discussion of these compounds form, see formation of coordination complexes.

✓ Example 8.2.1

Write the electronic configurations of:

a. neutral iron,
b. iron(II) ion, and
c. iron(III) ion.

Answer

The atomic number of iron is 26 so there are 26 protons in the species.

a. Fe: [Ar] $4s^2$ $3d^6$
b. Fe^{2+}: [Ar] $3d^6$
c. Fe^{3+}: [Ar] $3d^5$

Note that the s-orbital electrons are lost **first**, then the d-orbital electrons.

✓ Example 8.2.2

Determine the more stable configuration between the following pair:

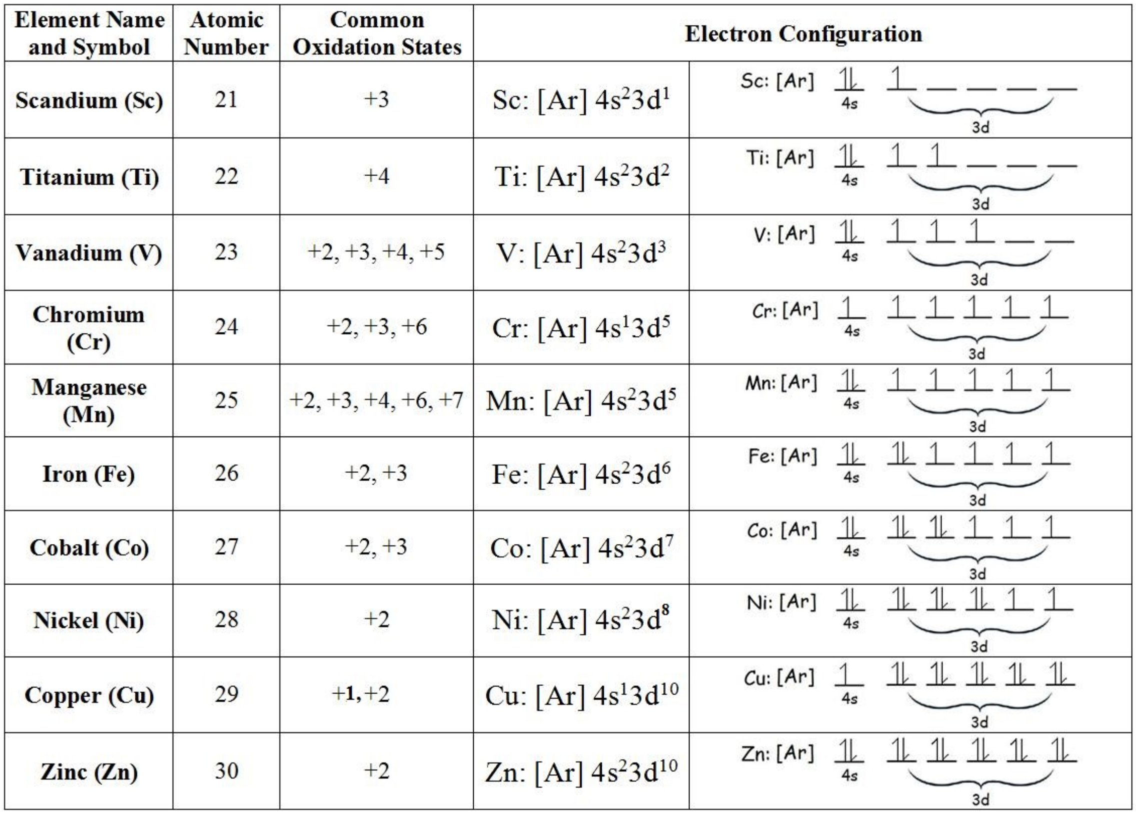
a. [Kr] $5s^2$ $4d^6$ vs. [Kr] $5s^1$ $4d^7$
b. Ag^{1+} vs. Ag^{2+}

Answer

a. This describes Ruthenium. There is only one 5s electron.
b. Once-oxidized silver ([Kr] $4d^{10}$) is more stable than twice- ([Kr] $4d^9$).

Multiple Oxidation States

Most transition metals have multiple oxidation states, since it is relatively easy to lose electron(s) for transition metals compared to the alkali metals and alkaline earth metals. Alkali metals have one electron in their valence s-orbital and their ions almost always have oxidation states of +1 (from losing a single electron). Similarly, alkaline earth metals have two electrons in their valences s-orbitals, resulting in ions with a +2 oxidation state (from losing both). However, transitions metals are more complex and exhibit a range of observable oxidation states due primarily to the removal of d-orbital electrons. The following chart describes the most common oxidation states of the period 3 elements.



Element Name and Symbol	Atomic Number	Common Oxidation States	Electron Configuration	
Scandium (Sc)	21	+3	Sc: [Ar] $4s^23d^1$	Sc: [Ar] ⇅ ↿ _ _ _ _ 4s 3d
Titanium (Ti)	22	+4	Ti: [Ar] $4s^23d^2$	Ti: [Ar] ⇅ ↿ ↿ _ _ _ 4s 3d
Vanadium (V)	23	+2, +3, +4, +5	V: [Ar] $4s^23d^3$	V: [Ar] ⇅ ↿ ↿ ↿ _ _ 4s 3d
Chromium (Cr)	24	+2, +3, +6	Cr: [Ar] $4s^13d^5$	Cr: [Ar] ↿ ↿ ↿ ↿ ↿ ↿ 4s 3d
Manganese (Mn)	25	+2, +3, +4, +6, +7	Mn: [Ar] $4s^23d^5$	Mn: [Ar] ⇅ ↿ ↿ ↿ ↿ ↿ 4s 3d
Iron (Fe)	26	+2, +3	Fe: [Ar] $4s^23d^6$	Fe: [Ar] ⇅ ⇅ ↿ ↿ ↿ ↿ 4s 3d
Cobalt (Co)	27	+2, +3	Co: [Ar] $4s^23d^7$	Co: [Ar] ⇅ ⇅ ⇅ ↿ ↿ ↿ 4s 3d
Nickel (Ni)	28	+2	Ni: [Ar] $4s^23d^8$	Ni: [Ar] ⇅ ⇅ ⇅ ⇅ ↿ ↿ 4s 3d
Copper (Cu)	29	+1, +2	Cu: [Ar] $4s^13d^{10}$	Cu: [Ar] ↿ ⇅ ⇅ ⇅ ⇅ ⇅ 4s 3d
Zinc (Zn)	30	+2	Zn: [Ar] $4s^23d^{10}$	Zn: [Ar] ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ 4s 3d

Scandium is one of the two elements in the first transition metal period which has only one oxidation state (zinc is the other, with an oxidation state of +2). All the other elements have at least two different oxidation states. Manganese, which is in the middle of the period, has the highest number of oxidation states, and indeed the highest oxidation state in the whole period since it has five unpaired electrons (see table below).

To help remember the stability of higher oxidation states for transition metals it is important to know the trend: the stability of the higher oxidation states progressively increases down a group. For example, in group 6, (chromium) Cr is most stable at a +3 oxidation state, meaning that you will not find many stable forms of Cr in the +4 and +5 oxidation states. By contrast, there are many stable forms of molybdenum (Mo) and tungsten (W) at +4 and +5 oxidation states.

✓ Example 8.2.3

What makes zinc stable as Zn^{2+}? What makes scandium stable as Sc^{3+}?

Answer

Zinc has the neutral configuration $[Ar]4s^23d^{10}$. Losing 2 electrons does not alter the complete d orbital. Neutral scandium is written as $[Ar]4s^23d^1$. Losing 3 electrons brings the configuration to the noble state with valence $3p^6$.

✓ Example 8.2.4

Why is iron almost always Fe^{2+} or Fe^{3+}?

Answer

Iron is written as $[Ar]4s^23d^6$. Losing 2 electrons from the s-orbital ($3d^6$) or 2 s- and 1 d-orbital ($3d^5$) electron are fairly stable oxidation states.

✓ Example 8.2.5

Write manganese oxides in a few different oxidation states. Which ones are possible and/or reasonable?

Answer

Although Mn^{+2} is the most stable ion for manganese, the d-orbital can be made to remove 0 to 7 electrons. Compounds of manganese therefore range from Mn(0) as $Mn_{(s)}$, Mn(II) as MnO, Mn(II,III) as Mn_3O_4, Mn(IV) as MnO_2, or manganese dioxide, Mn(VII) in the permanganate ion MnO_4^-, and so on.

Oxidation State of Transition Metals in Compounds

When given an ionic compound such as $AgCl$, you can easily determine the oxidation state of the transition metal. In this case, you would be asked to determine the oxidation state of silver (Ag). Since we know that chlorine (Cl) is in the halogen group of the periodic table, we then know that it has a charge of -1, or simply Cl^-. In addition, by seeing that there is no overall charge for $AgCl$, (which is determined by looking at the top right of the compound, i.e., $AgCl^{\#}$, where # represents the overall charge of the compound) we can conclude that silver (Ag) has an oxidation state of +1. This gives us Ag^+ and Cl^-, in which the positive and negative charge cancels each other out, resulting with an overall neutral charge; therefore +1 is verified as the oxidation state of silver (Ag).

✓ Example 8.2.6

Determine the oxidation state of cobalt in $CoBr_2$.

Answer

Similar to chlorine, bromine (Br) is also a halogen with an oxidation charge of -1 (Br^-). Since there are two bromines each with a charge of -1. In addition, we know that $CoBr_2$ has an overall neutral charge, therefore we can conclude that the cation (cobalt), Co must have an oxidation state of +2 to neutralize the -2 charge from the two bromine anions.

✓ Example 8.2.7

What is the oxidation state of zinc in $ZnCO_3$. (Note: the CO_3 anion has a charge state of -2)

Answer

Knowing that CO_3 has a charge of -2 and knowing that the overall charge of this compound is neutral, we can conclude that zinc has an oxidation state of +2. This gives us Zn^{2+} and CO_3^{-2}, in which the positive and negative charges from zinc and carbonate will cancel with each other, resulting in an overall neutral charge expected of a compound.

Polyatomic Transition Metal Ions

Consider the manganese (Mn) atom in the permanganate (MnO_4^-) ion. Since oxygen has an oxidation state of -2 and we know there are four oxygen atoms. In addition, this compound has an overall charge of -1; therefore the overall charge is not neutral in this example. Thus, since the oxygen atoms in the ion contribute a total oxidation state of -8, and since the overall charge of the ion is -1, the sole manganese atom must have an oxidation state of +7. This gives us Mn^{7+} and $4\ O^{2-}$, which will result as MnO_4^-.

> *This example also shows that manganese atoms can have an oxidation state of +7, which is the highest possible oxidation state for the fourth period transition metals.*

Manganese: A Case Study

Manganese is widely studied because it is an important reducing agent in chemical analysis and is also studied in biochemistry for catalysis and in metallurgy in fortifying alloys. In plants, manganese is required in trace amounts; stronger doses begin to react with enzymes and inhibit some cellular function. Due to manganese's flexibility in accepting many oxidation states, it becomes a good example to describe general trends and concepts behind electron configurations.

Figure 8.2.2: (left) A rough fragment of lustrous silvery metal (CC BY-SA 3.0; Tomihahndorf via Wikipedia) (right) Some of the Lascaux cave paintings use manganese-based pigments. (Public Domain; Prof saxx via Wikipedia)

Electron configurations of unpaired electrons are said to be **paramagnetic** and respond to the proximity of magnets. Fully paired electrons are **diamagnetic** and do not feel this influence. Manganese, in particular, has paramagnetic and diamagnetic orientations depending on what its oxidation state is.

Mn_2O_3 is manganese(III) oxide with manganese in the +3 state. 4 unpaired electrons means this complex is paramagnetic.

$$[\mathrm{Ar}]4s^0 3d^4$$

MnO_2 is manganese(IV) oxide, where manganese is in the +4 state. 3 unpaired electrons means this complex is less paramagnetic than Mn^{3+}.

$$[\mathrm{Ar}]4s^0 3d^3$$

$KMnO_4$ is potassium permanganate, where manganese is in the +7 state with no electrons in the 4s and 3d orbitals.

$$[\mathrm{Ar}]4s^0 3d^0$$

Since the 3p orbitals are all paired, this complex is diamagnetic.

Summary

Oxidation states of transition metals follow the general rules for most other ions, except for the fact that the d orbital is degenerated with the s orbital of the higher quantum number. Transition metals achieve stability by arranging their electrons accordingly and are oxidized, or they lose electrons to other atoms and ions. These resulting cations participate in the formation of coordination complexes or synthesis of other compounds.

Questions

Determine the oxidation states of the transition metals found in these neutral compounds. Note: The transition metal is underlined in the following compounds.

(A) Copper(I) Chloride: $CuCl$	(B) Copper(II) Nitrate: $Cu(NO_3)_2$	(C) Gold(V) Fluoride: AuF_5
(D) Iron(II) Oxide: FeO	(E) Iron(III) Oxide: Fe_2O_3	(F) Lead(II) Chloride: $PbCl_2$
(G) Lead(II) Nitrate: $Pb(NO_3)_2$	(H) Manganese(II) Chloride: $MnCl_2$	(I) Molybdenum trioxide: MoO_3
(J) Nickel(II) Hydroxide: $Ni(OH)_2$	(K) Platinum(IV) Chloride: $PtCl_4$	(L) Silver Sulfide: Ag_2S
(M) Tungsten(VI) Fluoride: WF_6	(N) Vanadium(III) Nitride: VN	(O) Zirconium Hydroxide: $Zr(OH)_4$

1. Determine the oxidation state of the transition metal for an overall non-neutral compound: Manganate (MnO_4^{2-})
2. Why do transition metals have a greater number of oxidation states than main group metals (i.e. alkali metals and alkaline earth metals)?
3. Which transition metal has the most number of oxidation states?
4. Why does the number of oxidation states for transition metals increase in the middle of the group?

5. What two transition metals have only one oxidation state?

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Contributors and Attributions

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8.3: Introduction to Coordination Chemistry

Learning Objectives

- To introduce complex ions and the basic principles of metal-ligand bonding

A complex ion has a metal ion at its center with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by coordinate (dative covalent) bonds (in some cases, the bonding is actually more complicated than that. The molecules or ions surrounding the central metal ion are called ligands. Simple ligands include water, ammonia and chloride ions.

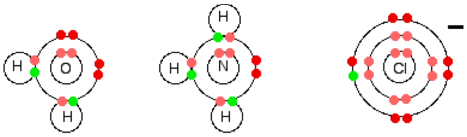


Figure 8.3.1: Simple Bohr diagram bonding in water, ammonia, and the chloride ion.

What all these have got in common is active lone pairs of electrons in the outer energy level. These are used to form co-ordinate bonds with the metal ion. All ligands are lone pair donors. In other words, all ligands function as Lewis bases.

Bonding in Simple Complex Ions

We are going to look in detail at the bonding in the complex ion formed when water molecules attach themselves to an aluminum ion to give $Al(H_2O)_6^{3+}$. Start by thinking about the structure of a naked aluminum ion before the water molecules bond to it.

Example 8.3.1: $Al(H_2O)_6^{3+}$

Aluminum has the electronic structure

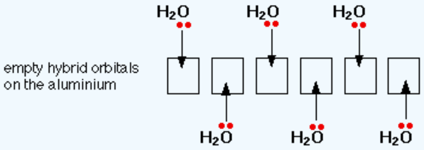
$$1s^22s^22p^63s^23p_x^1$$

When it forms an Al^{3+} ion it loses the 3-level electrons to leave

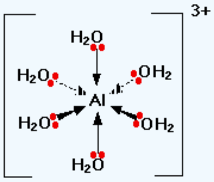
$$1s^22s^22p^6$$

That means that all the 3-level orbitals are now empty. The aluminium uses all six of these empty 3-level orbitals to accept lone pairs from six water molecules. It re-organizes (hybridizes) the 3s, the three 3p, and two of the 3d orbitals to produce six new orbitals all with the same energy.

You might wonder why it chooses to use six orbitals rather than four or eight or whatever. Six is the maximum number of water molecules that will fit around an aluminum ion (and most other metal ions) due to steric constraints. By making the maximum number of bonds, it releases most energy and so becomes most energetically stable.



Only one lone pair is shown on each water molecule. The other lone pair is pointing away from the aluminum and so isn't involved in the bonding. The resulting ion looks like this:



Because of the movement of electrons towards the center of the ion, the 3+ charge is no longer located entirely on the aluminum, but is now spread over the whole of the ion. Because the aluminum is forming 6 bonds, the co-ordination number of the aluminum is said to be 6. The co-ordination number of a complex ion counts the number of co-ordinate bonds being formed by the metal ion at its center.

In a simple case like this, that obviously also counts the number of ligands - but that is not necessarily so, as you will see later. Some ligands can form more than one co-ordinate bond with the metal ion.

✓ Example 8.3.2: $Fe(H_2O)_6^{3+}$

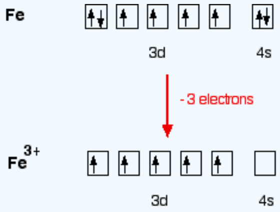
Iron has the electronic structure

$$1s^22s^22p^63s^23p^63d^64s^2$$

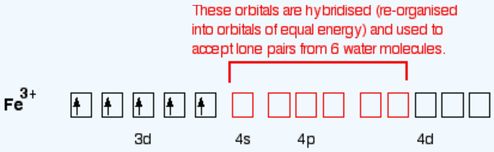
When it forms an Fe^{3+} ion it loses the 4s electrons and one of the 3d electrons to leave

$$1s^22s^22p^63s^23p^63d^5$$

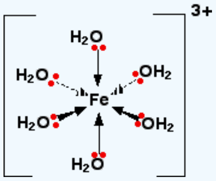
Looking at this as electrons-in-boxes, at the bonding level:



The single electrons in the 3d level are NOT involved in the bonding in any way. Instead, the ion uses 6 orbitals from the 4s, 4p and 4d levels to accept lone pairs from the water molecules. Before they are used, the orbitals are re-organized (hybridized) to produce 6 orbitals of equal energy.



Once the co-ordinate bonds have been formed, the ion looks exactly the same as the equivalent aluminium ion.



Because the iron is forming 6 bonds, the co-ordination number of the iron is 6.

✓ Example 8.3.3: $CuCl_4^{2-}$

This is a simple example of the formation of a complex ion with a negative charge.

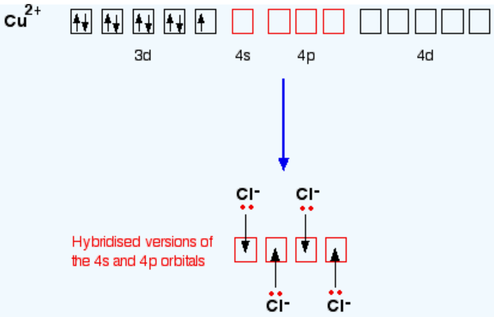
Copper has the electronic structure

$$1s^22s^22p^63s^23p^63d^{10}4s^1$$

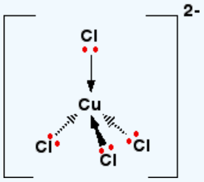
When it forms a Cu^{2+} ion it loses the 4s electron and one of the 3d electrons to leave

$$1s^22s^22p^63s^23p^63d^9$$

To bond the four chloride ions as ligands, the empty 4s and 4p orbitals are used (in a hybridized form) to accept a lone pair of electrons from each chloride ion. Because chloride ions are bigger than water molecules, you can't fit 6 of them around the central ion - that's why you only use 4.



Only one of the 4 lone pairs on each chloride ion is shown. The other three are pointing away from the copper ion, and aren't involved in the bonding. That gives you the complex ion:



The ion carries 2 negative charges overall. That comes from a combination of the 2 positive charges on the copper ion and the 4 negative charges from the 4 chloride ions. In this case, the co-ordination number of the copper is 4.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

8.4: Structures of Coordination Complexes

Learning Objectives

- To understand that there may be more than one way to arrange the same groups around the same atom with the same geometry (stereochemistry).

Two compounds that have the same formula and the same connectivity do not always have the same shape. There are two reasons why this may happen. In one case, the molecule may be flexible, so that it can twist into different shapes via rotation around individual sigma bonds. This phenomenon is called conformation, and it is covered in a different chapter. The second case occurs when two molecules appear to be connected the same way on paper, but are connected in two different ways in three dimensional space. These two, different molecules are called **stereoisomers**.

One simple example of stereoisomers from inorganic chemistry is diammine platinum dichloride, $(NH_3)_2PtCl_2$. This important compound is sometimes called "platin" for short. As the formula implies, it contains a platinum ion that is coordinated to two ammonia ligands and two chloride ligands (remember, a ligand in inorganic chemistry is an electron donor that is attached to a metal atom, donating a pair of electrons to form a bond).

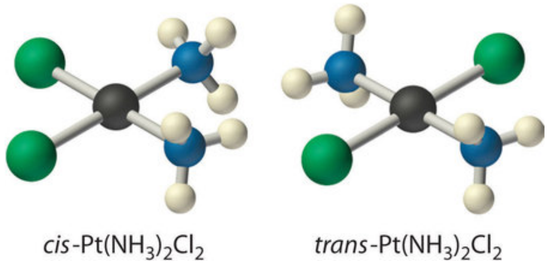


Figure 8.4.1: Two stereoisomers. The atoms are connected to each other in the same order, but differ in their three-dimensional relationships. (left) The cis-Platin compound is square planar at platinum and is flat when viewed from the edge, and square when viewed from the face. (right) The trans-Platin compound is connected in the same way as in cis-platin, and is still square planar, but there is a different 3-dimensional arrangement

Platin is an example of a coordination compound. The way the different pieces of coordination compounds bond together is discussed in the chapter of Lewis acids and bases. For reasons arising from molecular orbital interactions, platin has a square planar geometry at the platinum atom. That arrangement results in two possible ways the ligands could be connected. The two sets of like ligands could be connected on the same side of the square or on opposite corners.

These two arrangements result in two different compounds; they are isomers that differ only in three-dimensional space.

- The one with the two amines beside each other is called cis-platin.
- These two ligands are 90 degrees from each other.
- The one with the amines across from each other is trans-platin.
- These two ligands are 180 degrees from each other.

CIS/TRANS isomers have different physical properties

Although these two compounds are very similar, they have slightly different physical properties. Both are yellow compounds that decompose when heated to 270 degrees C, but trans-platin forms pale yellow crystals and is more soluble than cis-platin in water.

CIS/TRANS isomers have different biological properties

Cis-platin has clinical importance in the treatment of ovarian and testicular cancers. The biological mechanism of the drug's action was long suspected to involve binding of the platinum by DNA. Further details were worked out by MIT chemist Steve Lippard and graduate student Amy Rosenzweig in the 1990's. Inside the cell nucleus, the two ammines in cis-platin can be replaced by nitrogen donors from a DNA strand. To donate to the Lewis acidic platinum, the DNA molecule must bend slightly. Normally that bend is detected and repaired by proteins in the cell. However, ovarian and testicular cells happen to contain a protein that is just the right shape to fit around this slightly bent DNA strand. The DNA strand becomes lodged in the protein and can't be displaced, and so it is unable to bind with other proteins used in DNA replication. The cell becomes unable to replicate, and so cancerous growth is stopped.

Exercise 8.4.1

Draw the cis and trans isomers of the following compounds:

a. $(NH_3)_2IrCl(CO)$
b. $(H_3P)_2PtHBr$
c. $(AsH_3)_2PtH(CO)$

Exercise 8.4.2

Only one isomer of (tmeda)$PtCl_2$ is possible [tmeda = $(CH_3)_2NCH_2CH_2N(CH_3)_2$; both nitrogens connect to the platinum]. Draw this isomer and explain why the other isomer is not possible.

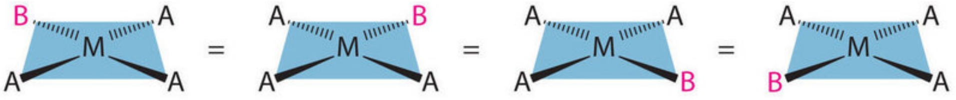
Geometric Isomers

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. Recall that in many cases more than one structure is possible for organic compounds with the same molecular formula; examples discussed previously include n-butane versus isobutane and cis-2-butene versus trans-2-butene. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique.

Planar Isomers

Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called geometrical isomers. They are most important for square planar and octahedral complexes.

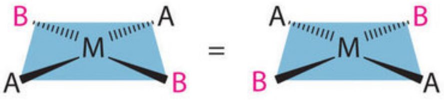
Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar MA_3B complex; hence only a single geometrical isomer is possible in this case (and in the analogous MAB_3 case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:



MA_3B square planar complex

For an MA_2B_2 complex, there are two possible isomers: either the A ligands can be adjacent to one another (cis), in which case the B ligands must also be cis, or the A ligands can be across from one another (trans), in which case the B ligands must also be trans. Even though it is possible to draw the cis isomer in four different ways and the trans isomer in two different ways, all members of each set are chemically equivalent:

MA_2B_2 square planar complex, *cis* isomer

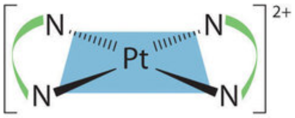


MA_2B_2 square planar complex, *trans* isomer

Figure 8.4.1).

The anticancer drug cisplatin and its inactive trans isomer. Cisplatin is especially effective against tumors of the reproductive organs, which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin.

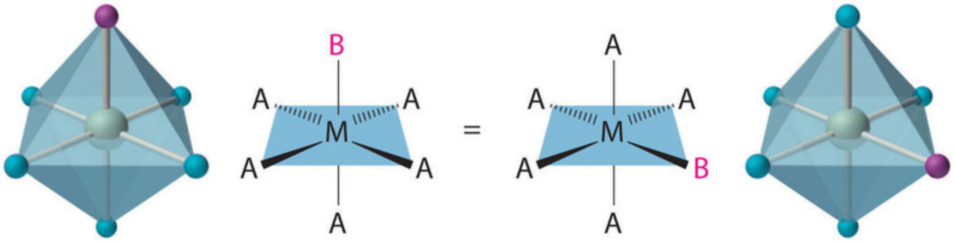
Square planar complexes that contain symmetrical bidentate ligands, such as $[Pt(en)_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:



$[Pt(en)_2]^{2+}$

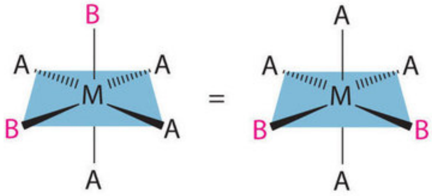
Octahedral Isomers

Octahedral complexes also exhibit cis and trans isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five (MA_5B). Even though we usually draw an octahedron in a way that suggests that the four “in-plane” ligands are different from the two “axial” ligands, in fact all six vertices of an octahedron are equivalent. Consequently, no matter how we draw an MA_5B structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an MA_5B structure are as follows:

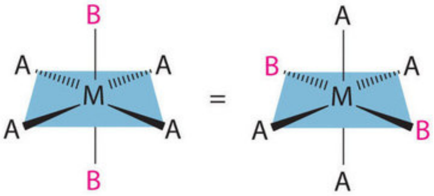


MA_5B octahedral complex

If two ligands in an octahedral complex are different from the other four, giving an MA_4B_2 complex, two isomers are possible. The two B ligands can be cis or trans. Cis- and trans-$[Co(NH_3)_4Cl_2]Cl$ are examples of this type of system:

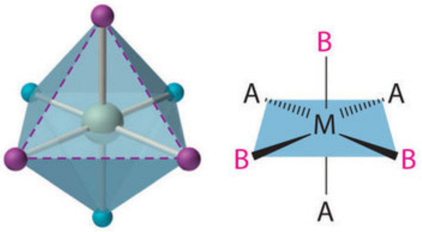


MA_4B_2 octahedral complex, *cis* isomer

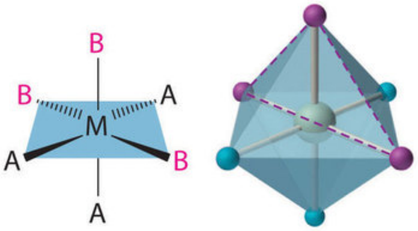


MA_4B_2 octahedral complex, *trans* isomer

Replacing another A ligand by B gives an MA_3B_3 complex for which there are also two possible isomers. In one, the three ligands of each kind occupy opposite triangular faces of the octahedron; this is called the fac isomer (for facial). In the other, the three ligands of each kind lie on what would be the meridian if the complex were viewed as a sphere; this is called the mer isomer (for meridional):



MA_3B_3 octahedral complex, *fac* isomer



MA_3B_3 octahedral complex, *mer* isomer

Example 8.4.1

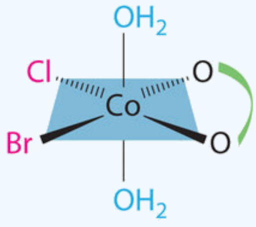
Draw all the possible geometrical isomers for the complex $[Co(H_2O)_2(ox)BrCl]^-$, where ox is $^-O_2CCO_2{}^-$, which stands for oxalate.

Given: formula of complex

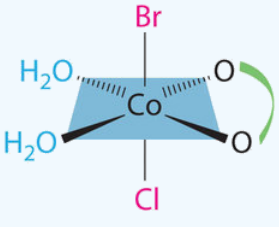
Asked for: structures of geometrical isomers

Solution

This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (cis) positions, and four monodentate ligands, two of which are identical (H_2O). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be trans. Thus either the water ligands can be trans to one another or the two halide ligands can be trans to one another, giving the two geometrical isomers shown here:

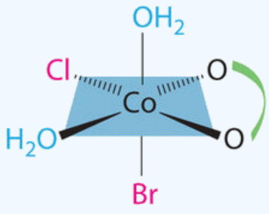


H_2O's *trans*

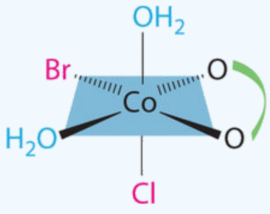


Br, Cl *trans*

In addition, two structures are possible in which one of the halides is trans to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens. Exchanging the chloride and bromide ligands gives the other, in which the bromide ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens:



H_2O's *cis*; Br, Cl *cis*;
Cl *trans* to O



H_2O's *cis*; Br, Cl *cis*;
Br *trans* to O

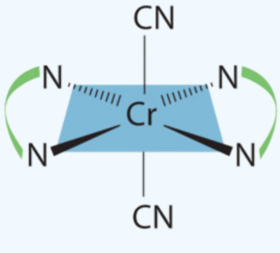
This complex can therefore exist as four different geometrical isomers.

Exercise 8.4.1

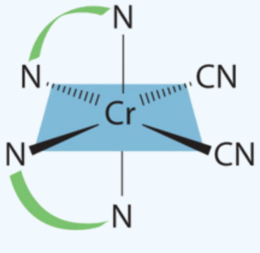
Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.

Answer

Two geometrical isomers are possible: trans and cis.



trans



cis

Summary

Many metal complexes form isomers, which are two or more compounds with the same formula but different arrangements of atoms. Structural isomers differ in which atoms are bonded to one another, while geometrical isomers differ only in the arrangement of ligands around the metal ion. Ligands adjacent to one another are cis, while ligands across from one another are trans.

Contributors and Attributions

- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

8.5: Crystal Field Theory: Optical and Magnetic Properties

Learning Objectives

- To understand how crystal field theory explains the electronic structures and colors of metal complexes.

One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit. In this section, we describe crystal field theory (CFT), a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature. Even though this assumption is clearly not valid for many complexes, such as those that contain neutral ligands like CO, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy. The Learning Objective of this Module is to understand how crystal field theory explains the electronic structures and colors of metal complexes.

d-Orbital Splittings

CFT focuses on the interaction of the five (n − 1)d orbitals with ligands arranged in a regular array around a transition-metal ion. We will focus on the application of CFT to octahedral complexes, which are by far the most common and the easiest to visualize. Other common structures, such as square planar complexes, can be treated as a distortion of the octahedral model. According to CFT, an octahedral metal complex forms because of the electrostatic interaction of a positively charged metal ion with six negatively charged ligands or with the negative ends of dipoles associated with the six ligands. In addition, the ligands interact with one other electrostatically. As you learned in our discussion of the valence-shell electron-pair repulsion (VSEPR) model, the lowest-energy arrangement of six identical negative charges is an octahedron, which minimizes repulsive interactions between the ligands.

We begin by considering how the energies of the d orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall that the five d orbitals are initially degenerate (have the same energy). If we distribute six negative charges uniformly over the surface of a sphere, the d orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the d orbitals (Figure $8.5.1a$). Placing the six negative charges at the vertices of an octahedron does not change the average energy of the d orbitals, but it does remove their degeneracy: the five d orbitals split into two groups whose energies depend on their orientations. As shown in Figure $8.5.1b$, the d_{z^2} and $d_{x^2-y^2}$ orbitals point directly at the six negative charges located on the x, y, and z axes. Consequently, the energy of an electron in these two orbitals (collectively labeled the e_g orbitals) will be greater than it will be for a spherical distribution of negative charge because of increased electrostatic repulsions. In contrast, the other three d orbitals (d_{xy}, d_{xz}, and d_{yz}, collectively called the t_{2g} orbitals) are all oriented at a 45° angle to the coordinate axes, so they point between the six negative charges. The energy of an electron in any of these three orbitals is lower than the energy for a spherical distribution of negative charge.

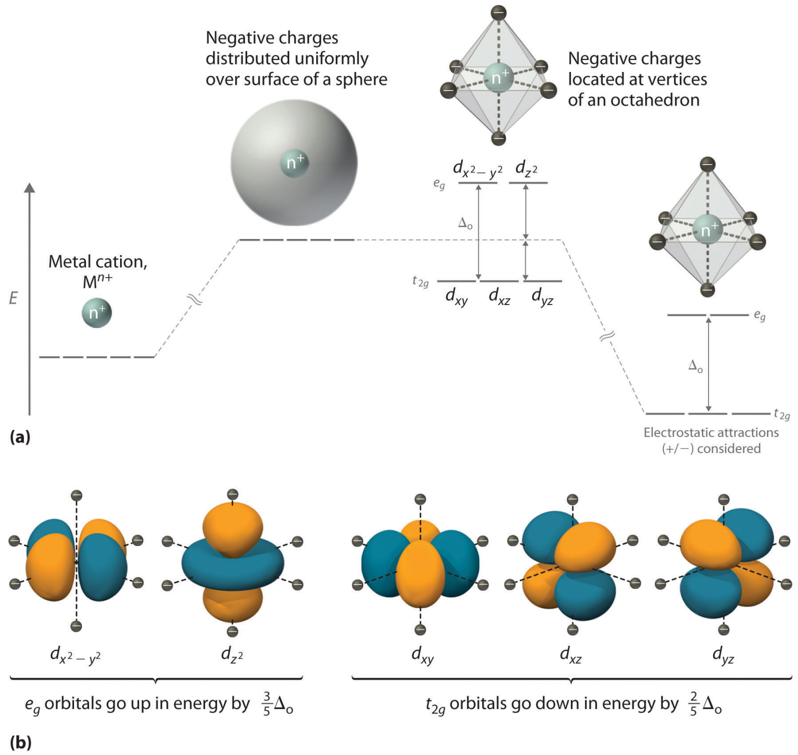


Figure 8.5.1: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies. (a) Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of −1 at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the $d_{x^2-y^2}$ and d_{z^2} orbitals increase in energy, while the, d_{xy}, d_{xz}, and d_{yz} orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a −6 charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. (b) The two e_g orbitals (left) point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of negative charge. In contrast, the three t_{2g} orbitals (right) point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge.

The difference in energy between the two sets of d orbitals is called the crystal field splitting energy (Δ_o), where the subscript o stands for octahedral. As we shall see, the magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. (Crystal field splitting energy also applies to tetrahedral complexes: Δ_t.) It is important to note that the splitting of the d orbitals in a crystal field does not change the total energy of the five d orbitals: the two e_g orbitals increase in energy by $0.6\Delta_o$, whereas the three t_{2g} orbitals decrease in energy by $0.4\Delta_o$. Thus the total change in energy is

$$2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0.$$

> *Crystal field splitting does not change the total energy of the d orbitals.*

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the d orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the d orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five d orbitals without affecting their splitting (as shown at the far right in Figure 8.5.1*a*).

Electronic Structures of Metal Complexes

We can use the d-orbital energy-level diagram in Figure 8.5.1 to predict electronic structures and some of the properties of transition-metal complexes. We start with the Ti^{3+} ion, which contains a single d electron, and proceed across the first row of the transition metals by adding a single electron at a time. We place additional electrons in the lowest-energy orbital available, while keeping their spins parallel as required by Hund's rule. As shown in Figure 24.6.2, for d^1–d^3 systems—such as $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, and $[Cr(H_2O)_6]^{3+}$, respectively—the electrons successively occupy the three degenerate t_{2g} orbitals with their spins parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex $[Cr(H_2O)_6]^{3+}$, for example, by saying that the chromium ion has a d^3 electron configuration or, more succinctly, Cr^{3+} is a d^3 ion.

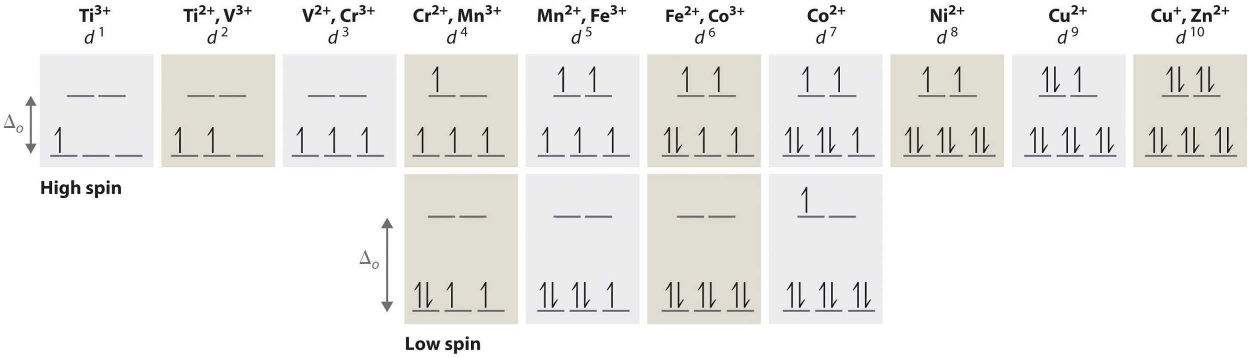


Figure 8.5.2: The Possible Electron Configurations for Octahedral d^n Transition-Metal Complexes (n = 1–10). Two different configurations are possible for octahedral complexes of metals with d^4, d^5, d^6, and d^7 configurations; the magnitude of Δ_o determines which configuration is observed.

When we reach the d^4 configuration, there are two possible choices for the fourth electron: it can occupy either one of the empty e_g orbitals or one of the singly occupied t_{2g} orbitals. Recall that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the spin-pairing energy (P). If Δ_o is less than P, then the lowest-energy arrangement has the fourth electron in one of the empty e_g orbitals. Because this arrangement results in four unpaired electrons, it is called a high-spin configuration, and a complex with this electron configuration, such as the $[Cr(H_2O)_6]^{2+}$ ion, is called a high-spin complex. Conversely, if Δ_o is greater than P, then the lowest-energy arrangement has the fourth electron in one of the occupied t_{2g} orbitals. Because this arrangement results in only two unpaired electrons, it is called a low-spin configuration, and a complex with this electron configuration, such as the $[Mn(CN)_6]^{3-}$ ion, is called a low-spin complex. Similarly, metal ions with the d^5, d^6, or d^7 electron configurations can be either high spin or low spin, depending on the magnitude of Δ_o.

In contrast, only one arrangement of d electrons is possible for metal ions with d^8–d^{10} electron configurations. For example, the $[Ni(H_2O)_6]^{2+}$ ion is d^8 with two unpaired electrons, the $[Cu(H_2O)_6]^{2+}$ ion is d^9 with one unpaired electron, and the $[Zn(H_2O)_6]^{2+}$ ion is d^{10} with no unpaired electrons.

> *If Δ_o is less than the spin-pairing energy, a high-spin configuration results. Conversely, if Δ_o is greater, a low-spin configuration forms.*

Factors That Affect the Magnitude of Δ_o

The magnitude of Δ_o dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ_o (i.e., $\Delta_o > P$) yield a low-spin complex, whereas small values of Δ_o (i.e., $\Delta_o < P$) produce a high-spin complex. As we noted, the magnitude of Δ_o depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of Δ_o for some representative transition-metal complexes are given in Table 8.5.1.

Table 8.5.1: Crystal Field Splitting Energies for Some Octahedral (Δ_o)* and Tetrahedral (Δ_t) Transition-Metal Complexes

Octahedral Complexes	**Δ_o (cm^{-1})**	**Octahedral Complexes**	**Δ_o (cm^{-1})**	**Tetrahedral Complexes**	**Δ_t (cm^{-1})**
$[Ti(H_2O)_6]^{3+}$	20,300	$[Fe(CN)_6]^{4-}$	32,800	VCl_4	9010
$[V(H_2O)_6]^{2+}$	12,600	$[Fe(CN)_6]^{3-}$	35,000	$[CoCl_4]^{2-}$	3300
$[V(H_2O)_6]^{3+}$	18,900	$[CoF_6]^{3-}$	13,000	$[CoBr_4]^{2-}$	2900
$[CrCl_6]^{3-}$	13,000	$[Co(H_2O)_6]^{2+}$	9300	$[CoI_4]^{2-}$	2700

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.

Octahedral Complexes	**Δ_o (cm^{-1})**	**Octahedral Complexes**	**Δ_o (cm^{-1})**	**Tetrahedral Complexes**	**Δ_t (cm^{-1})**
$[Cr(H_2O)_6]^{2+}$	13,900	$[Co(H_2O)_6]^{3+}$	27,000		
$[Cr(H_2O)_6]^{3+}$	17,400	$[Co(NH_3)_6]^{3+}$	22,900		
$[Cr(NH_3)_6]^{3+}$	21,500	$[Co(CN)_6]^{3-}$	34,800		
$[Cr(CN)_6]^{3-}$	26,600	$[Ni(H_2O)_6]^{2+}$	8500		
$Cr(CO)_6$	34,150	$[Ni(NH_3)_6]^{2+}$	10,800		
$[MnCl_6]^{4-}$	7500	$[RhCl_6]^{3-}$	20,400		
$[Mn(H_2O)_6]^{2+}$	8500	$[Rh(H_2O)_6]^{3+}$	27,000		
$[MnCl_6]^{3-}$	20,000	$[Rh(NH_3)_6]^{3+}$	34,000		
$[Mn(H_2O)_6]^{3+}$	21,000	$[Rh(CN)_6]^{3-}$	45,500		
$[Fe(H_2O)_6]^{2+}$	10,400	$[IrCl_6]^{3-}$	25,000		
$[Fe(H_2O)_6]^{3+}$	14,300	$[Ir(NH_3)_6]^{3+}$	41,000		

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, Inorganic Chemistry, 2nd ed. (New York: W. H. Freeman and Company, 1994).

Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both factors decrease the metal–ligand distance, which in turn causes the negatively charged ligands to interact more strongly with the d orbitals. Consequently, the magnitude of Δ_o increases as the charge on the metal ion increases. Typically, Δ_o for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for $[V(H_2O)_6]^{2+}$, Δ_o = 11,800 cm^{-1}; for $[V(H_2O)_6]^{3+}$, Δ_o = 17,850 cm^{-1}.

Principal Quantum Number of the Metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of Δ_o increases with increasing principal quantum number: Δ_o (3d) < Δ_o (4d) < Δ_o (5d). The data for hexaammine complexes of the trivalent group 9 metals illustrate this point:

$$[Co(NH_3)_6]^{3+}: \Delta_o = 22{,}900\ cm^{-1}$$

$$[Rh(NH_3)_6]^{3+}: \Delta_o = 34{,}100\ cm^{-1}$$

$$[Ir(NH_3)_6]^{3+}: \Delta_o = 40{,}000\ cm^{-1}$$

The increase in Δ_o with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions.

The Nature of the Ligands

Experimentally, it is found that the Δ_o observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of Δ_o decreases as the size of the donor atom increases. For example, Δ_o values for halide complexes generally decrease in the order F^- > Cl^- > Br^- > I− because smaller, more localized charges, such as we see for F^-, interact more strongly with the d orbitals of the metal ion. In addition, a small neutral ligand with a highly localized lone pair, such as NH_3, results in significantly larger Δ_o values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as F^-. The experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series, shown here in order of decreasing Δ_o:

$$\underbrace{CO \approx CN^- > NO_2^-}_{\text{strong-field ligands}} > en > NH_3 > \underbrace{SCN^- > H_2O > oxalate^{2-}}_{\text{intermediate-field ligands}} > OH^- > F > acetate^- > \underbrace{Cl^- > Br^- > I^-}_{\text{weak-field ligands}}$$

The values of Δ_o listed in Table 8.5.1 illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

> *The largest Δ_o splittings are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.*

Colors of Transition-Metal Complexes

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy d orbital to a higher-energy d orbital, which is called a d–d transition (Figure 24.6.3). For a photon to effect such a transition, its energy must be equal to the difference in energy between the two d orbitals, which depends on the magnitude of Δ_o.

Figure 8.5.3: A d–d Transition. In a d–d transition, an electron in one of the t_{2g} orbitals of an octahedral complex such as the $[Cr(H_2O)_6]^{3+}$ ion absorbs a photon of light with energy equal to Δ_o, which causes the electron to move to an empty or singly occupied e_g orbital.

Recall that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the color wheel. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of Δ_o, which depends on the structure of the complex. For example, the complex $[Cr(NH_3)_6]^{3+}$ has strong-field ligands and a relatively large Δ_o. Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the $[Cr(H_2O)_6]^{3+}$ ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color.

We can now understand why emeralds and rubies have such different colors, even though both contain Cr^{3+} in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different (Al_2O_3 in rubies and $Be_3Al_2Si_6O_{18}$ in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the d orbital–ligand interactions and makes Δ_o relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large $[Si_6O_{18}]^{12-}$ silicate rings; this results in decreased d orbital–ligand interactions and a smaller Δ_o. Consequently, emeralds absorb light of a longer wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.

Gem-quality crystals of ruby and emerald. The colors of both minerals are due to the presence of small amounts of Cr^{3+} impurities in octahedral sites in an otherwise colorless metal oxide lattice.

Crystal Field Stabilization Energies

Recall that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of d orbitals (the t_{2g} orbitals) is selectively populated by electrons, then the stability of the complex increases. For example, the single d electron in a d^1 complex such as $[Ti(H_2O)_6]^{3+}$ is located in one of the t_{2g} orbitals. Consequently, this complex will be more stable than expected on purely electrostatic grounds by $0.4\Delta_o$. The additional stabilization of a metal complex by selective population of the lower-energy d orbitals is called its crystal field stabilization energy (CFSE). The CFSE of a complex can be calculated by multiplying the number of electrons in t_{2g} orbitals by the energy of those orbitals ($-0.4\Delta_o$), multiplying the number of electrons in e_g orbitals by the energy of those orbitals ($+0.6\Delta_o$), and summing the two. Table 8.5.2 gives CFSE values for octahedral complexes with different d electron configurations. The CFSE is highest for low-spin d^6 complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. The other low-spin configurations also have high CFSEs, as does the d^3 configuration.

Table 8.5.2: CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δo)

	High Spin		CFSE (Δ_o)	Low Spin		CFSE (Δ_o)
d^0			0			
d^1	↿		0.4			
d^2	↿ ↿		0.8			
d^3	↿ ↿ ↿		1.2			
d^4	↿ ↿ ↿	↿	0.6	↿⇂ ↿ ↿		1.6
d^5	↿ ↿ ↿	↿ ↿	0.0	↿⇂ ↿⇂ ↿		2.0
d^6	↿⇂ ↿ ↿	↿ ↿	0.4	↿⇂ ↿⇂ ↿⇂		2.4
d^7	↿⇂ ↿⇂ ↿	↿ ↿	0.8	↿⇂ ↿⇂ ↿⇂	↿	1.8
d^8	↿⇂ ↿⇂ ↿⇂	↿ ↿	1.2			
d^9	↿⇂ ↿⇂ ↿⇂	↿⇂ ↿	0.6			
d^{10}	↿⇂ ↿⇂ ↿⇂	↿⇂ ↿⇂	0.0			

CFSEs are important for two reasons. First, the existence of CFSE nicely accounts for the difference between experimentally measured values for bond energies in metal complexes and values calculated based solely on electrostatic interactions. Second, CFSEs represent relatively large amounts of energy (up to several hundred kilojoules per mole), which has important chemical consequences.

> *Octahedral d^3 and d^8 complexes and low-spin d^6, d^5, d^7, and d^4 complexes exhibit large CFSEs.*

✓ Example 8.5.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[CoF_6]^{3-}$
b. $[Rh(CO)_2Cl_2]^-$

Given: complexes

Asked for: structure, high spin versus low spin, and the number of unpaired electrons

Strategy:

a. From the number of ligands, determine the coordination number of the compound.
b. Classify the ligands as either strong field or weak field and determine the electron configuration of the metal ion.
c. Predict the relative magnitude of Δ_o and decide whether the compound is high spin or low spin.
d. Place the appropriate number of electrons in the d orbitals and determine the number of unpaired electrons.

Solution

a. A With six ligands, we expect this complex to be octahedral.

B The fluoride ion is a small anion with a concentrated negative charge, but compared with ligands with localized lone pairs of electrons, it is weak field. The charge on the metal ion is +3, giving a d^6 electron configuration.

C Because of the weak-field ligands, we expect a relatively small Δ_o, making the compound high spin.

D In a high-spin octahedral d^6 complex, the first five electrons are placed individually in each of the d orbitals with their spins parallel, and the sixth electron is paired in one of the t_{2g} orbitals, giving four unpaired electrons.

b. A This complex has four ligands, so it is either square planar or tetrahedral.

B C Because rhodium is a second-row transition metal ion with a d^8 electron configuration and CO is a strong-field ligand, the complex is likely to be square planar with a large Δ_o, making it low spin. Because the strongest d-orbital interactions are along the x and y axes, the orbital energies increase in the order $d_{z^2}d_{yz}$, and d_{xz} (these are degenerate); d_{xy}; and $d_{x^2-y^2}$.

D The eight electrons occupy the first four of these orbitals, leaving the $d_{x^2-y^2}$. orbital empty. Thus there are no unpaired electrons.

Exercise 8.5.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[Mn(H_2O)_6]^{2+}$
b. $[PtCl_4]^{2-}$

Answers

a. octahedral; high spin; five
b. square planar; low spin; no unpaired electrons

Summary

Crystal field theory, which assumes that metal–ligand interactions are only electrostatic in nature, explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. Crystal field theory (CFT) is a bonding model that explains many properties of transition metals that cannot be explained using valence bond theory. In CFT, complex formation is assumed to be due to electrostatic interactions between a central metal ion and a set of negatively charged ligands or ligand dipoles arranged around the metal ion. Depending on the arrangement of the ligands, the d orbitals split into sets of orbitals with different energies. The difference between the energy levels in an octahedral complex is called the crystal field splitting energy (Δ_o), whose magnitude depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. The spin-pairing energy (P) is the increase in energy that occurs when an electron is added to an already occupied orbital. A high-spin configuration occurs when the Δ_o is less than P, which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the Δ_o is greater than P, which produces complexes with the minimum number of unpaired electrons possible. Strong-field ligands interact strongly with the d orbitals of the metal ions and give a large Δ_o, whereas weak-field ligands interact more weakly and give a smaller Δ_o. The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT.

8.6: Optical Properties and the Spectrochemical Series

Learning Objectives

- To get a simple overview of the origin of color and magnetism in complex ions.

Electromagnetic radiation is a form of energy that is produced by oscillating electric and magnetic disturbance, or by the movement of electrically charged particles traveling through a vacuum or matter. Electron radiation is released as photons, which are bundles of light energy that travel at the speed of light as quantized harmonic waves. This energy is then grouped into categories based on its wavelength into the electromagnetic spectrum and have certain characteristics, including amplitude, wavelength, and frequency (Figure 8.6.1).

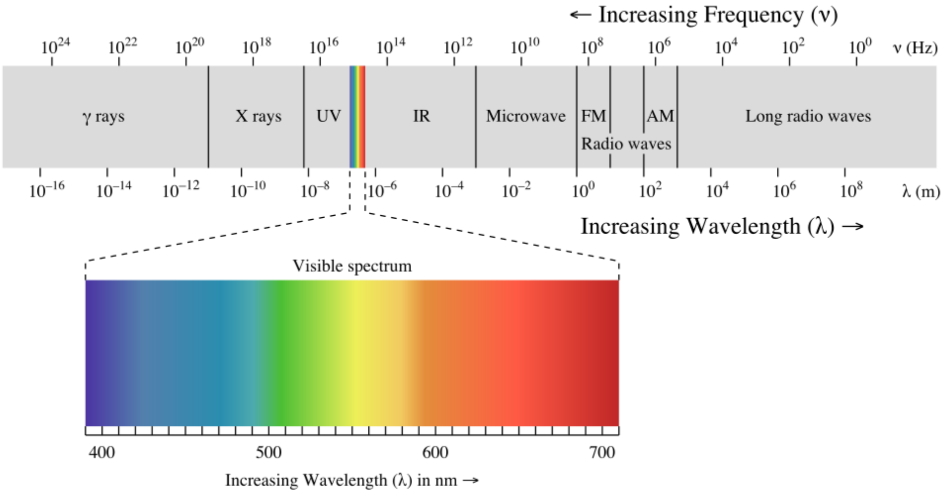


Figure 8.6.1: Electromagnetic spectrum with light highlighted. (CC -SA-BY 2.0 unported; Philip Ronan).

General properties of all electromagnetic radiation include:

1. Electromagnetic radiation can travel through empty space, while most other types of waves must travel through some sort of substance. For example, sound waves need either a gas, solid, or liquid to pass through to be heard.
2. The speed of light (c) is always a constant (2.99792458 x 10^8 m s^{-1}).
3. Wavelengths (λ) are measured between the distances of either crests or troughs.

The energy of a photon is expressed by Planck's law in terms of the frequency (u) of the photon

$$E = hu \tag{8.6.1}$$

since $\lambda u = c$ for all light Plancks law can be also expressed in terms of the wavelength of the photon

$$E = hu = \frac{hc}{\lambda} \tag{8.6.2}$$

If white light is passed through a prism, it splits into all the colors of the rainbow (Figure 8.6.2). Visible light is simply a small part of an electromagnetic spectrum most of which we cannot see - gamma rays, X-rays, infra-red, radio waves and so on. Each of these has a particular wavelength, ranging from 10^{-16} meters for gamma rays to several hundred meters for radio waves. Visible light has wavelengths from about 400 to 750 nm (1 nanometer = 10^{-9} meters).

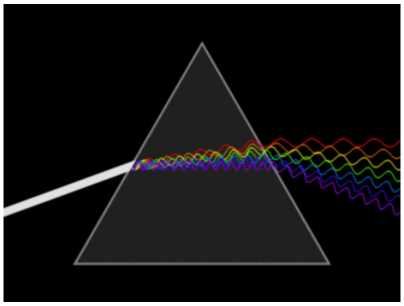
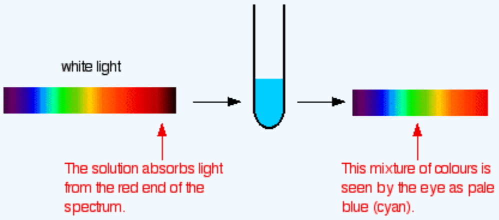


Figure 8.6.2: A triangular prism, dispersing light; waves shown to illustrate the differing wavelengths of light. (Public Domain; Lucas V. Barbosa).

✓ Example 8.6.1: Blue Color of Copper (II) Sulfate in Solution

If white light (ordinary sunlight, for example) passes through copper(II) sulfate solution, some wavelengths in the light are absorbed by the solution. Copper(II) ions in solution absorb light in the red region of the spectrum. The light which passes through the solution and out the other side will have all the colors in it except for the red. We see this mixture of wavelengths as pale blue (cyan). The diagram gives an impression of what happens if you pass white light through copper(II) sulfate solution.



Working out what color you will see is not easy if you try to do it by imagining "mixing up" the remaining colors. You would not have thought that all the other colors apart from some red would look cyan, for example. Sometimes what you actually see is quite unexpected. Mixing different wavelengths of light doesn't give you the same result as mixing paints or other pigments. You can, however, sometimes get some estimate of the color you would see using the idea of complementary colors.

Origin of Colors

The process of absorption involves the excitation of the valence electrons in the molecule typically from the low lying level called the Highest Occupied Molecular Orbital (HOMO) into a higher lying state called the the Lowest Unoccupied Molecular Orbital (**LUMO**). When this HOMO and LUMO transition (Figure 8.6.3) involves the absorption of visible light, the sample is colored.

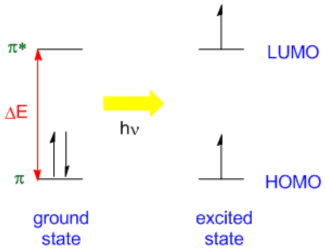


Figure 8.6.4: The general electron excitation process from a HOMO to a LUMO.

The HOMO-LUMO energy difference

$$\Delta E = E_{HOMO} - E_{LUMO} \tag{8.6.3}$$

depends on the nature of the molecule and can be connected to the wavelength of the light absorbed

$$\Delta E = hu = \frac{hc}{\lambda} \tag{8.6.4}$$

> *Equation 8.6.4 is the most important equation in the field of light-matter interactions (spectroscopy).*

As Example 8.6.1 demonstrated, when white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown below. Here, complementary colors are diametrically opposite each other (Figure 8.6.5). Thus, absorption of 420-430 nm light renders a substance yellow, and absorption of 500-520 nm light makes it red. Green is unique in that it can be created by absorption close to 400 nm as well as absorption near 800 nm.

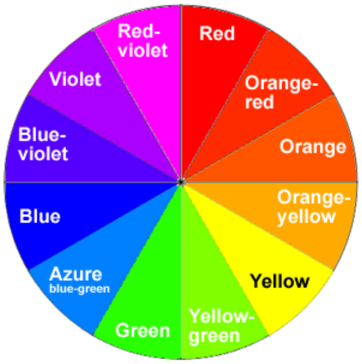


Figure 8.6.5: The color wheel used to identify the color of species.

Colors directly opposite each other on the color wheel are said to be complementary colors. Blue and yellow are complementary colors; red and cyan are complementary; and so are green and magenta. Mixing together two complementary colors of light will give you white light. What this all means is that if a particular color is absorbed from white light, what your eye detects by mixing up all the other wavelengths of light is its complementary color. Copper(II) sulfate solution is pale blue (cyan) because it absorbs light in the red region of the spectrum and cyan is the complementary color of red (Table 8.6.1).

Table 8.6.1: The Visible Spectrum

Color	Wavelength (nm)	ΔE HOMO - LUMO gap (eV)
UV	100 - 400	12.4 - 3.10
Violet	400 - 425	3.10 - 2.92
Blue	425 - 492	2.92 - 2.52
Green	492 - 575	2.52 - 2.15
Yellow	575 - 585	2.15 - 2.12
Orange	585 - 647	2.12 - 1.92
Red	647 - 700	1.92 - 1.77
Near IR	700 - 10,000	1.77 - 0.12

If the compound absorbs in one region of the spectra, it appears with the opposite (complementary) color, since all of the absorbed color has been removed. For example:

- the material absorbs violet light ⇒ color is yellow
- the material absorbs blue light ⇒ color is orange
- the material absorbs yellow-green light ⇒ color is red-violet

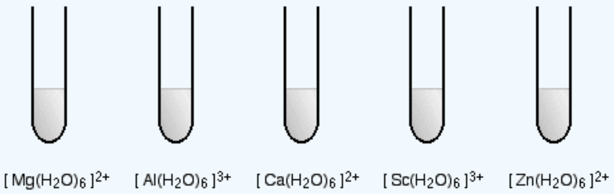
The Origin of Color in Complex Ions

We often casually talk about the transition metals as being those in the middle of the Periodic Table where d orbitals are being filled, but these should really be called d block elements rather than transition elements (or metals). The definition of a transition metal is one which forms one or more stable ions which have incompletely filled d orbitals. Zinc with the electronic structure [Ar] $3d^{10}4s^2$ does not count as a transition metal whichever definition you use. In the metal, it has a full 3d level. When it forms an ion, the 4s electrons are lost - again leaving a completely full 3d level. At the other end of the row, scandium ([Ar] $3d^1 4s^2$) does not really counts as a transition metal either. Although there is a partially filled d level in the metal, when it forms its ion, it loses all three outer electrons. The Sc^{3+} ion does not count as a transition metal ion because its 3d level is empty.

✓ Example 8.6.3: Hexaaqua Metal Ions

The diagrams show the approximate colors of some typical hexaaqua metal ions, with the formula $[\ M(H_2O)_6\ ]^{n+}$. The charge on these ions is typically 2+ or 3+.

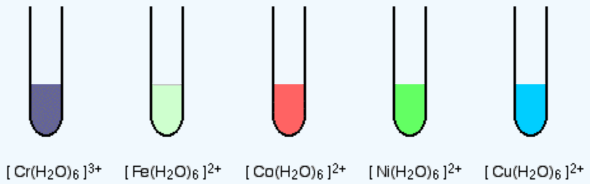
- Non-transition metal ions



These ions are all colorless.

Ions are [Mg(H2O)6] two plus, [Al(H2O)6] three plus, [Ca(H2O)6] two plus, [Sc(H2O)6] three plus, and [Zn(H2O)6] two plus

- Transition metal ions



Ions are [Cr(h2O)6] three plus, [Fe(H20)6] two plus, [Co(H2O)6] two plus, [Ni(H2O)6] two plus, and [Cu[H2O)6] two plus.

The corresponding transition metal ions are colored. Some, like the hexaaquamanganese(II) ion (not shown) and the hexaaquairon(II) ion, are quite faintly colored - but they are colored.

So, what causes transition metal ions to absorb wavelengths from visible light (causing color) whereas non-transition metal ions do not? And why does the color vary so much from ion to ion? This is discussed in the next sections.

Magnetism

The magnetic moment of a system measures the strength and the direction of its magnetism. The term itself usually refers to the magnetic dipole moment. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic forms: including paramagnetism, and diamagnetism, ferromagnetism, and anti-ferromagnetism. Only the first two are introduced below.

Paramagnetism

Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. Hund's Rule states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can spin in either direction, they display magnetic moments in any direction. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, O_2 is a good example of paramagnetism (described via molecular orbital theory). The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet:

A chemical demonstration of the paramagnetism of oxygen, as shown by the attraction of liquid oxygen to a magnet. Carleton University, Ottawa, Canada.

As shown in the video, molecular oxygen (O_2 is paramagnetic and is attracted to the magnet. Incontrast, Molecular nitrogen, N_2, however, has no unpaired electrons and it is diamagnetic (this concept is discussed below); it is therefore unaffected by the magnet.

There are some exceptions to the paramagnetism rule; these concern some transition metals, in which the unpaired electron is not in a d-orbital. Examples of these metals include Sc^{3+}, Ti^{4+}, Zn^{2+}, and Cu^{+}. These metals are the not defined as paramagnetic: they are considered diamagnetic because all d-electrons are paired. Paramagnetic compounds sometimes display bulk magnetic properties due to the clustering of the metal atoms. This phenomenon is known as ferromagnetism, but this property is not discussed here.

Diamagnetism

Diamagnetic substances are characterized by paired electrons—except in the previously-discussed case of transition metals, there are no unpaired electrons. According to the Pauli Exclusion Principle which states that no two identical electrons may take up the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out; thus there is no net magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure $8.6.6$.

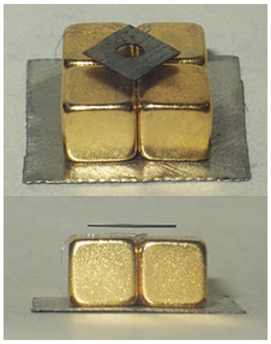


Figure $8.6.6$: Levitating pyrolytic carbon: A small (~6 mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5 mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). from Wikipedia.

How to Tell if a Substance is Paramagnetic or Diamagnetic

The magnetic form of a substance can be determined by examining its electron configuration: if it shows unpaired electrons, then the substance is paramagnetic; if all electrons are paired, the substance is diamagnetic. This process can be broken into four steps:

1. Find the electron configuration

2. Draw the valence orbitals
3. Look for unpaired electrons
4. Determine whether the substance is paramagnetic (one or more unpaired electrons) or diamagnetic (all electrons paired)

✓ Example 8.6.4: Chlorine atoms

Are chlorine atoms paramagnetic or diamagnetic?

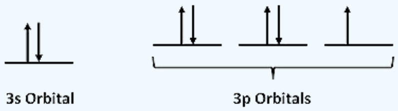
Solution

Step 1: Find the electron configuration

For Cl atoms, the electron configuration is $3s^2 3p^5$

Step 2: Draw the valence orbitals

Ignore the core electrons and focus on the valence electrons only.



Step 3: Look for unpaired electrons

There is one unpaired electron.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

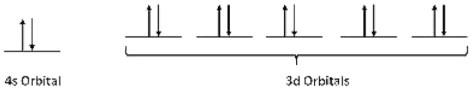
Since there is an unpaired electron, Cl atoms are paramagnetic (but is quite weak).

Example 2: Zinc Atoms

Step 1: Find the electron configuration

For Zn atoms, the electron configuration is $4s^2 3d^{10}$

Step 2: Draw the valence orbitals



Step 3: Look for unpaired electrons

There are no unpaired electrons.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Because there are no unpaired electrons, Zn atoms are diamagnetic.

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8.7: Bonding in Coordination Complexes

Ligands can be further characterized as monodentate, bidentate, tridentate etc. where the concept of teeth **(dent)** is introduced. Monodentate ligands bind through only one donor atom. Monodentate means "one-toothed." The halides, phosphines, ammonia and amines seen previously are monodentate ligands. Bidentate ligands bind through two donor sites. Bidentate means "two-toothed." An example of a bidentate ligand is ethylenediamine. It can bind to a metal via two donor atoms at once.

Figure 8.7.1: The hypothetical "lobster ligand" binds to the Ni^{2+} via two donor sites.

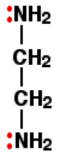
Bidentate binding allows a ligand to bind more tightly. Tridentate ligands, which bind through three donors, can bind even more tightly, and so on. This phenomenon is generally called the "**chelate effect**." This term comes from the Greek chelos, meaning "crab." A crab does not have any teeth at all, but it does have two claws for tightly holding onto something for a couple of reasons. A very simple analogy is that, if you are holding something with two hands rather than one, you are not as likely to drop it.

Complex metal ions containing more complicated ligands

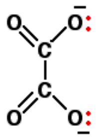
In the examples previously disccussed, each ligand only forms one bond with the central metal ion to give the complex ion. Such a ligand is said to be unidentate. That means literally that it only has one tooth! It only has one pair of electrons that it can use to bond to the metal - any other lone pairs are pointing in the wrong direction. Some ligands, however, have rather more teeth! These are known generally as multidentate or polydentate ligands, but can be broken down into a number of different types.

Bidentate ligands

Bidentate ligands have two lone pairs, both of which can bond to the central metal ion. The two commonly used examples are 1,2-diaminoethane (old name: ethylenediamine - often given the abbreviation "en"), and the ethanedioate ion (old name: oxalate).

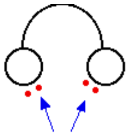


1,2-diaminoethane



ethanedioate ion

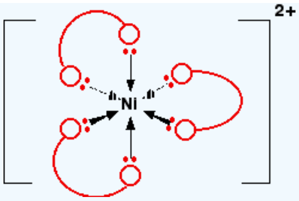
In the ethanedioate ion, there are lots more lone pairs than the two shown, but these are the only ones we are interested in. You can think of these bidentate ligands rather as if they were a pair of headphones, carrying lone pairs on each of the "ear pieces". These will then fit snuggly around a metal ion.



These can both be used to form co-ordinate bonds with the same metal ion.

Example 8.7.1: $Ni(NH_2CH_2CH_2NH_2)_3^{2+}$

You might find this abbreviated to $[Ni(en)_3]^{2+}$. The structure of the ion looks like this:



In this case, the "ear pieces" are the nitrogen atoms of the NH2 groups - and the "bit that goes over your head " is the $-CH_2CH_2-$ group. If you were going to draw this in an exam, you would obviously want to draw it properly - but for learning purposes, drawing all the atoms makes the diagram look unduly complicated!

Notice that the arrangement of the bonds around the central metal ion is exactly the same as it was with the ions with 6 water molecules attached. The only difference is that this time each ligand uses up two of the positions - at right angles to each other.

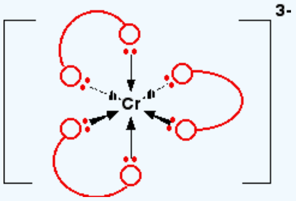
Because the nickel is forming 6 co-ordinate bonds, the coordination number of this ion is 6, despite the fact that it is only joined to 3 ligands. Coordination number counts the number of bonds, not the number of ligands.

✓ Example 5: $Cr(C_2O_4)_3^{3-}$

This is the complex ion formed by attaching 3 ethanedioate (oxalate) ions to a chromium(III) ion. The shape is exactly the same as the previous nickel complex. The only real difference is the number of charges. The original chromium ion carried 3+ charges, and each ethanedioate ion carried -2, i.e.,

$$(+3)+(3\times -2)=-3.$$

The structure of the ion looks like this:

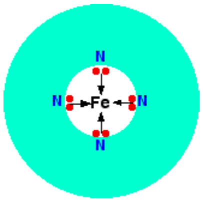


Again, if you drew this in an exam, you would want to show all the atoms properly. If you need to be able to do this, practice drawing it so that it looks clear and tidy! Refer back to the diagram of the ethanedioate ion further up the page to help you.

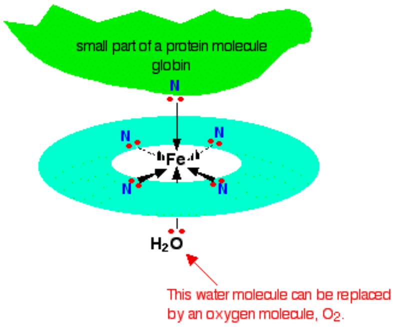
A Quadridentate Ligand

A quadridentate ligand has four lone pairs, all of which can bond to the central metal ion. An example of this occurs in haemoglobin (American: hemoglobin). The functional part of this is an iron(II) ion surrounded by a complicated molecule called heme. This is a sort of hollow ring of carbon and hydrogen atoms, at the center of which are 4 nitrogen atoms with lone pairs on them. Heme is one of a group of similar compounds called porphyrins. They all have the same sort of ring system, but with different groups attached to the outside of the ring. You aren't going to need to know the exact structure of the haem at this level.

We could simplify the heme with the trapped iron ion as:



Each of the lone pairs on the nitrogen can form a co-ordinate bond with the iron(II) ion - holding it at the center of the complicated ring of atoms. The iron forms 4 co-ordinate bonds with the heme, but still has space to form two more - one above and one below the plane of the ring. The protein globin attaches to one of these positions using a lone pair on one of the nitrogens in one of its amino acids. The interesting bit is the other position.



This water molecule can be replaced by an oxygen molecule, O_2.

Figure 8.7.2: Overall, the complex ion has a co-ordination number of 6 because the central metal ion is forming 6 co-ordinate bonds.

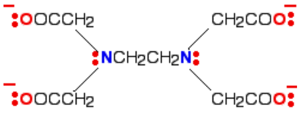
The water molecule which is bonded to the bottom position in the diagram is easily replaced by an oxygen molecule (again via a lone pair on one of the oxygens in O_2) - and this is how oxygen gets carried around the blood by the haemoglobin. When the oxygen gets to where it is needed, it breaks away from the haemoglobin which returns to the lungs to get some more.

Carbon Monoxide Poisoning

You probably know that carbon monoxide is poisonous because it reacts with hemeoglobin. It bonds to the same site that would otherwise be used by the oxygen - but it forms a very stable complex. The carbon monoxide doesn't break away again, and that makes that hemeoglobin molecule useless for any further oxygen transfer.

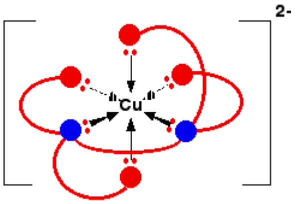
A Hexadentate Ligand

A hexadentate ligand has 6 lone pairs of electrons - all of which can form co-ordinate bonds with the same metal ion. The best example is EDTA. The diagram shows the structure of the ion with the important atoms and lone pairs picked out.



the EDTA^{4-} ion

The EDTA ion entirely wraps up a metal ion using all 6 of the positions that we have seen before. The co-ordination number is again 6 because of the 6 co-ordinate bonds being formed by the central metal ion. The diagram below shows this happening with a copper(II) ion. Here is a simplified version. Make sure that you can see how this relates to the full structure above.



the [Cu(EDTA)]$^{2-}$ ion

The overall charge, of course, comes from the 2+ on the original copper(II) ion and the 4- on the $EDTA^{4-}$ ion.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

SECTION OVERVIEW

Unit 3: The States of Matter

An General Chemistry Libretexts Textmap organized around the textbook
Principles of Modern Chemistry
by Oxtoby, Gillis, and Campion

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI
XVII XVIII XIX XX XXI XXII XXIII • **Homework Exercises**

Template:HideTOC

A state of matter is one of the distinct forms that matter takes on. Three states of matter are observable in everyday life: solid, liquid, and gas.Historically, the distinction between state is made based on qualitative differences in properties. Solids maintain a fixed volume and shape, with component particles (atoms, molecules or ions) close together and fixed into place. Liquids maintain a fixed volume, but has a variable shape that adapts to fit its container. Its particles are still close together like in solids, but move freely. Gases have both variable volume and shape and adapt to fit its container. Gas particles are neither close together nor fixed in place.

CHAPTER OVERVIEW

9: The Gaseous State

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI
XVII XVIII XIX XX XXI XXII XXIII ● **Homework Exercises**

Template:HideTOC

Some of the first real breakthroughs in the study of chemistry happened in the study of the gaseous state. In gases, the volume of the actual gas particles is but a tiny fraction of the total volume that the gas occupies. This allowed early chemists to relate parameters such as volume and the number of gas particles, leading to the development of the mole concept. As we have seen in previous chapters, the notion of a chemical mole allows us to do quantitative chemistry and lead us to the point where we can routinely address reaction stoichiometry, etc. In this chapter, we will visit some of the early observations that lead to our current understand of gasses and how they behave. We will see how the relationships between pressure and volume; volume and temperature and volume and moles lead to the ideal gas laws and how these simple rules can allow us to do quantitative calculations in the gas phase.

Thumbnail: The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion with a lot of distance between the particles.

9.1: The Chemistry of Gases

9.2: Pressure and Temperature of Gases

9.3: The Ideal Gas Law

9.4: Mixtures of Gases

9.5: The Kinetic Theory of Gases

9.6: A Deeper Look: Distribution of Energy among Molecules

9.7: Real Gases: Intermolecular Forces

9.8: A Deeper Look: Molecular Collisions and Rate Processes

CHAPTER OVERVIEW

10: Solids, Liquids, and Phase Transitions

Gas, liquid, and solid are known as the three states of matter or material, but each of solid and liquid states may exist in one or more forms. Thus, another term is required to describe the various forms, and the term phase is used. Each distinct form is called a phase, but the concept of phase defined as a homogeneous portion of a system, extends beyond a single material, because a phase may also involve several materials. A solid has a definite shape and volume. A liquid has a definite volume but it takes the shape of a container whereas a gas fills the entire volume of a container. You already know that diamond and graphite are solids made up of the element carbon. They are two phases of carbon, but both are solids.Solids are divided into subclasses of amorphous (or glassy) solids and crystalline solids. Arrangements of atoms or molecules in crystalline solids are repeated regularly over a very long range of millions of atoms, but their arrangements in amorphous solids are somewhat random or short range of say some tens or hundreds of atoms. In general, there is only one liquid phase of a material. However, there are two forms of liquid helium, each have some unique properties. Thus, the two forms are different (liquid) phases of helium. At a definite temperature and pressure, the two phases co-exist.

00: Front Matter

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10: Solids, Liquids, and Phase Transitions

Table of Contents

10.1: Bulk Properties of Liquids - Molecular Interpretation

Learning Objectives

- To describe the unique properties of liquids.
- To know how and why the vapor pressure of a liquid varies with temperature.
- To understand that the equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.

Although you have been introduced to some of the interactions that hold molecules together in a liquid, we have not yet discussed the consequences of those interactions for the bulk properties of liquids. We now turn our attention to four unique properties of liquids that intimately depend on the nature of intermolecular interactions:

1. surface tension,
2. capillary action,
3. viscosity, and
4. boiling point.

Surface Tension

If liquids tend to adopt the shapes of their containers, then why do small amounts of water on a freshly waxed car form raised droplets instead of forming a thin, continuous film? The answer lies in a property called **surface tension**, which depends on intermolecular forces. Surface tension is the energy required to increase the surface area of a liquid by a unit amount and varies greatly from liquid to liquid based on the nature of the intermolecular forces, e.g., water with hydrogen bonds has a surface tension of $7.29 \times 10^{-2} J/m^2$ (at 20°C), while mercury with metallic (electrostatic) bonds has as surface tension that is 6.5-times greater: $4.86 \times 10^{-1} J/m^2$ (at 20°C).

Figure $10.1.1$ presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads. A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.

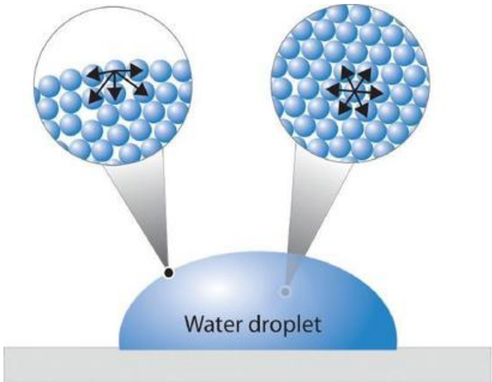


Figure 10.1.1: A Representation of Surface Tension in a Liquid. Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces. (CC BY-SA-NC; anonymous)

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it “floats,” even though steel is much denser than water. Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking. This is better demonstrated in the zero-gravity conditions of space (Figure 10.1.2).

Figure 10.1.2: The Effects of the High Surface Tension of Liquid Water. The Full video can be found at https://youtu.be/o8TssbmY-GM.

Such phenomena are manifestations of surface tension, which is defined as the energy required to increase the surface area of a liquid by a specific amount. Surface tension is therefore measured as energy per unit area, such as joules per square meter (J/m^2). The values of the surface tension of some representative liquids are listed in Table 10.1.2. Note the correlation between the surface tension of a liquid and the strength of the intermolecular forces: the stronger the intermolecular forces, the higher the surface tension. For example, water, with its strong intermolecular hydrogen bonding, has one of the highest surface tension values of any liquid, whereas low-boiling-point organic molecules, which have relatively weak intermolecular forces, have much lower surface tensions. Mercury is an apparent anomaly, but its very high surface tension is due to the presence of strong metallic bonding.

Table 10.1.2: Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids

Substance	Surface Tension (× 10^{-3} J/m^2)	Viscosity (mPa•s)	Vapor Pressure (mmHg)	Normal Boiling Point (°C)
Organic Compounds				
diethyl ether	17	0.22	531	34.6
n-hexane	18	0.30	149	68.7
acetone	23	0.31	227	56.5
ethanol	22	1.07	59	78.3
ethylene glycol	48	16.1	~0.08	198.9
Liquid Elements				
bromine	41	0.94	218	58.8
mercury	486	1.53	0.0020	357
Water				
0°C	75.6	1.79	4.6	—
20°C	72.8	1.00	17.5	—
60°C	66.2	0.47	149	—
100°C	58.9	0.28	760	—

Adding soaps and detergents that disrupt the intermolecular attractions between adjacent water molecules can reduce the surface tension of water. Because they affect the surface properties of a liquid, soaps and detergents are called surface-active agents, or surfactants. In the 1960s, US Navy researchers developed a method of fighting fires aboard aircraft carriers using "foams," which are aqueous solutions of fluorinated surfactants. The surfactants reduce the surface tension of water below that of fuel, so the fluorinated solution is able to spread across the burning surface and extinguish the fire. Such foams are now used universally to fight large-scale fires of organic liquids.

Surface Energies and Surface Tension

Any material - solid, liquid or (non-ideal) gas - wants to bond to itself. This is why condensed phase materials "sticks" together in the first place. However, a surface disrupts this bonding, and so incurs an energy penalty. This is why liquids in zero gravity ball up into spherical drops (Figure $10.1.2$) - the sphere is the shape with the lowest surface area for a fixed volume. We can describe this *surface energy* with dimensions of energy per unit area, which is the amount of extra energy needed to create new surface or extend a surface (e.g., cracking a solid or parting a liquid). Hence, surface tension is typically given in J/m^2 units (Table $10.1.2$).

Capillary Action

Intermolecular forces also cause a phenomenon called capillary action, which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure $10.1.3$. When a glass capillary is put into a dish of water, water is drawn up into the tube. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises. The height of the water does *not* depend on the angle at which the capillary is tilted.

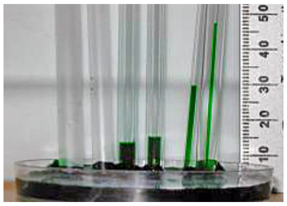


Figure $10.1.3$: The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters. (Dr. Clay Robinson, PhD, West Texas A&M University)

Capillary action is the net result of two opposing sets of forces: cohesive forces, which are the intermolecular forces that hold a liquid together, and adhesive forces, which are the attractive forces between a liquid and the substance that composes the capillary.

- Cohesive forces bind molecules of the same type together
- Adhesive forces bind a substance to a surface

Water has both strong adhesion to glass, which contains polar SiOH groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (part (a) in Figure $10.1.4$). The upper surface of a liquid in a tube is called the meniscus, and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex (Figure $10.1.4b$).

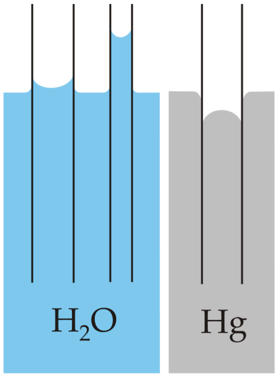


Figure 10.1.4: The Phenomenon of Capillary Action. Capillary action of water compared to mercury, in each case with respect to a polar surface such as glass. (a) This drawing illustrates the shape of the meniscus and the relative height of a mercury column when a glass capillary is put into liquid mercury. The meniscus is convex and the surface of the liquid inside the tube is *lower* than the level of the liquid outside the tube. (b) Because water adheres strongly to the polar surface of glass, it has a concave meniscus, whereas mercury, which does not adhere to the glass, has a convex meniscus. (CC BY-SA 3.0; MesserWoland via Wikipedia)

Fluids and nutrients are transported up the stems of plants or the trunks of trees by capillary action. Plants contain tiny rigid tubes composed of cellulose, to which water has strong adhesion. Because of the strong adhesive forces, nutrients can be transported from the roots to the tops of trees that are more than 50 m tall. Cotton towels are also made of cellulose; they absorb water because the tiny tubes act like capillaries and “wick” the water away from your skin. The moisture is absorbed by the entire fabric, not just the layer in contact with your body.

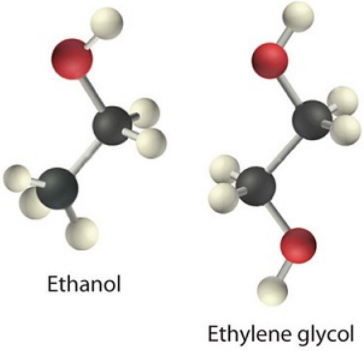
> *Polar substances are drawn up a glass capillary and generally have concave meniscuses and nonpolar substances general avoid the capillary and exhibit convex meniscuses.*

Viscosity

Viscosity (η) is the resistance of a liquid to flow. Some liquids, such as gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The two most common methods for evaluating the viscosity of a liquid are

1. to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and
2. to measure the time it takes steel balls to fall through a given volume of the liquid.

The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa•s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table 10.1.1 and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($HOCH_2CH_2OH$), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.



Comparison of structures of ethanol (left) with ethylene glycol (right). (CC BY-SA-NC; anonymous)

There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become “tangled” with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

> *Viscosity increases as intermolecular interactions or molecular size increases.*

Application: Motor Oils

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine must effectively lubricate under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an engine in the heat of the Mojave Desert in August. Viscosity decreases rapidly with increasing temperatures because the kinetic energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing (Table 10.1.3). As a result, an oil that is thin enough to be a good lubricant in a cold engine will become too “thin” (have too low a viscosity) to be effective at high temperatures.

Viscosity of motor Oils. youtu.be/V5a4kP-5Jiw

The viscosity of motor oils is described by an SAE (Society of Automotive Engineers) rating ranging from SAE 5 to SAE 50 for engine oils: the lower the number, the lower the viscosity. So-called *single-grade oils* can cause major problems. If they are viscous enough to work at high operating temperatures (SAE 50, for example), then at low temperatures, they can be so viscous that a car is difficult to start or an engine is not properly lubricated. Consequently, most modern oils are *multigrade*, with designations such as SAE 20W/50 (a grade used in high-performance sports cars), in which case the oil has the viscosity of an SAE 20 oil at subzero temperatures (hence the W for winter) and the viscosity of an SAE 50 oil at high temperatures. These properties are achieved by a careful blend of additives that modulate the intermolecular interactions in the oil, thereby controlling the temperature dependence of the viscosity. Many of the commercially available oil additives “for improved engine performance” are highly viscous materials that increase the viscosity and effective SAE rating of the oil, but overusing these additives can cause the same problems experienced with highly viscous single-grade oils.

Table 10.1.3: Dynamic Viscosity (N s/m^2)

SAE	Temperature (^oC)			
	0	20	50	100
10	0.31	0.079	0.020	0.005
20	0.72	0.170	0.033	0.007
30	1.53	0.310	0.061	0.010

SAE	Temperature (^oC)			
	0	20	50	100
40	2.61	0.430	0.072	0.012
50	3.82	0.630	0.097	0.015

✓ Example 10.1.1

Based on the nature and strength of the intermolecular cohesive forces and the probable nature of the liquid–glass adhesive forces, predict what will happen when a glass capillary is put into a beaker of SAE 20 motor oil. Will the oil be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)? (Hint: the surface of glass is lined with Si–OH groups.)

Given: substance and composition of the glass surface

Asked for: behavior of oil and the shape of meniscus

Strategy:

A. Identify the cohesive forces in the motor oil.
B. Determine whether the forces interact with the surface of glass. From the strength of this interaction, predict the behavior of the oil and the shape of the meniscus.

Solution:

A Motor oil is a nonpolar liquid consisting largely of hydrocarbon chains. The cohesive forces responsible for its high boiling point are almost solely London dispersion forces between the hydrocarbon chains.

B Such a liquid cannot form strong interactions with the polar Si–OH groups of glass, so the surface of the oil inside the capillary will be lower than the level of the liquid in the beaker. The oil will have a convex meniscus similar to that of mercury.

? Exercise 10.1.1

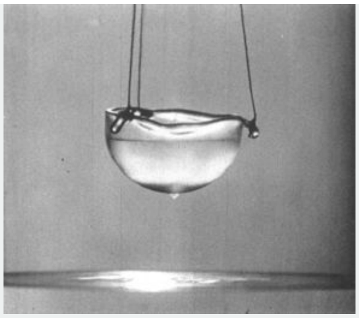
Predict what will happen when a glass capillary is put into a beaker of ethylene glycol. Will the ethylene glycol be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)?

Answer

Capillary action will pull the ethylene glycol up into the capillary. The meniscus will be concave.

Oddity of Science: Superfluid Helium-4

Superfluid helium-4 is the superfluid form of helium-4, an isotope of the element helium. A superfluid is a state of matter in which the matter behaves like a fluid with zero viscosity. The substance, which looks like a normal liquid, flows without friction past any surface, which allows it to continue to circulate over obstructions and through pores in containers which hold it, subject only to its own inertia.



The liquid helium is in the superfluid phase. A thin invisible film creeps up the inside wall of the cup and down on the outside. A drop forms. It will fall off into the liquid helium below. This will repeat until the cup is empty - provided the liquid remains superfluid. (Public Domain; Alfred Leitner).

Many ordinary fluids, like alcohol or petroleum, creep up solid walls, driven by their surface tension. However, in the case of superfluid helium-4, the flow of the liquid in the layer is not restricted by its viscosity but by a critical velocity which is about 20 cm/s. This is a fairly high velocity so superfluid helium can flow relatively easily up the wall of containers, over the top, and down to the same level as the surface of the liquid inside the container. In a container, lifted above the liquid level, it forms visible droplets as seen above.

Boiling Points

The **vapor pressure** of a liquid is defined as the pressure exerted by a vapor in equilibrium with its condensed phases (solid or liquid) at a given temperature in a closed system (discussed in more detail in next Sections of Chapter). As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point of the liquid. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure 10.1.8 are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm.

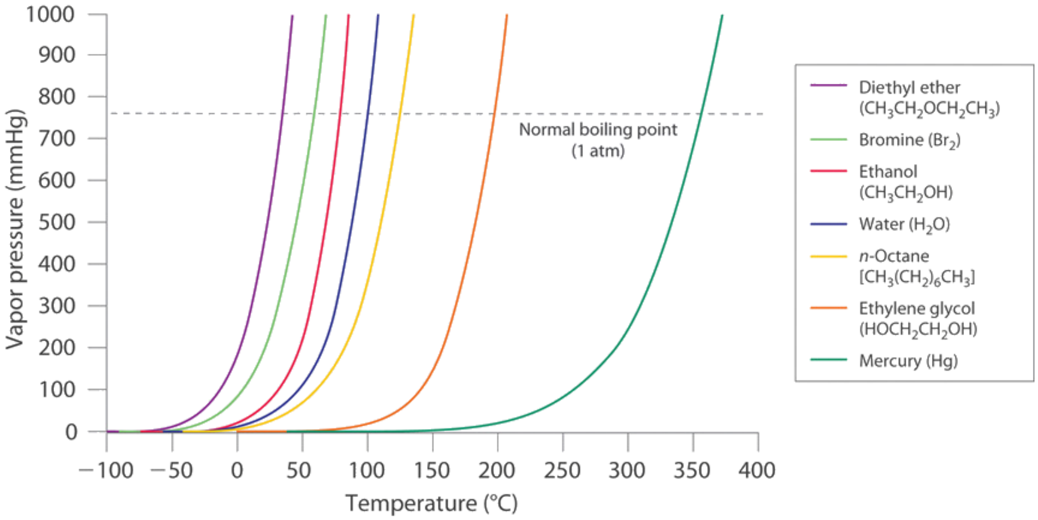


Figure 10.1.8: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC; anonymous)

Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils below 100°C.

Table 10.1.4: The Boiling Points of Water at Various Locations on Earth

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Mt. Everest, Nepal/Tibet	29,028	240	70

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Bogota, Colombia	11,490	495	88
Denver, Colorado	5280	633	95
Washington, DC	25	759	100
Dead Sea, Israel/Jordan	−1312	799	101.4

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 mmHg, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 mmHg in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C, respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table $10.1.4$ lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a "three-minute egg" may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

> *As pressure increases, the boiling point of a liquid increases and vice versa.*

✓ Example 10.1.2: Boiling Mercury

Use Figure $10.1.8$ to estimate the following.

a. the boiling point of water in a pressure cooker operating at 1000 mmHg
b. the pressure required for mercury to boil at 250°C

Mercury boils at 356 °C at room pressure. To see video go to www.youtube.com/watch?v=0iizsbXWYoo

Given: data in Figure $10.1.8$, pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure $10.1.8$ and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.
B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

a. The vapor pressure curve of water intersects the P = 1000 mmHg line at about 110°C; this is therefore the boiling point of water at 1000 mmHg.
b. The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx 75$ mmHg. Hence this is the pressure required for mercury to boil at 250°C.

? Exercise 10.1.2: Boiling Ethylene Glycol

Ethylene glycol is an organic compound primarily used as a raw material in the manufacture of polyester fibers and fabric industry, and polyethylene terephthalate resins (PET) used in bottling. Use the data in Figure $10.1.8$ to estimate the following.

a. the normal boiling point of ethylene glycol
b. the pressure required for diethyl ether to boil at 20°C.

Answer a

200°C

Answer b

450 mmHg

Summary

Surface tension, capillary action, boiling points, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions. **Surface tension** is the energy required to increase the surface area of a liquid by a given amount. The stronger the intermolecular interactions, the greater the surface tension. **Surfactants** are molecules, such as soaps and detergents, that reduce the surface tension of polar liquids like water. **Capillary action** is the phenomenon in which liquids rise up into a narrow tube called a capillary. It results when **cohesive forces**, the intermolecular forces in the liquid, are weaker than **adhesive forces**, the attraction between a liquid and the surface of the capillary. The shape of the **meniscus**, the upper surface of a liquid in a tube, also reflects the balance between adhesive and cohesive forces. The **viscosity** of a liquid is its resistance to flow. Liquids that have strong intermolecular forces tend to have high viscosities. The **boiling point** of a liquid is the temperature when the **vapor pressure** of the liquid equals the external pressure, or the atmospheric pressure in the case of an open container.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

10.2: Intermolecular Forces - Origins in Molecular Structure

Learning Objectives

- To describe the intermolecular forces in liquids.

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids. In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

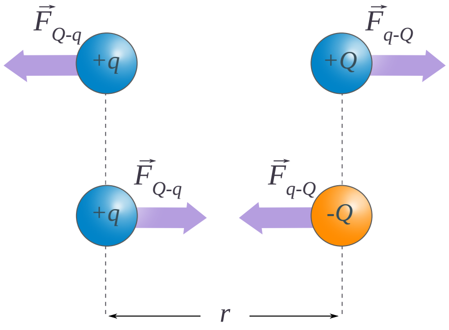
> The properties of liquids are intermediate between those of gases and solids but are more similar to solids.

Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Coulombic Interactions

Through various experiments, Charles Augustin de Coulomb found a way to explain the interactions between charged particles, which in turn helped to explain where the stabilities and instabilities of various particles come from. While the entities that hold atoms together within a molecule can be attributed to bonds, the forces that create these bonds can be explained by Coulomb Forces. Thus, the physical basis behind the bonding of two atoms can be explained.

Coulomb’s findings indicate that like charges repel each other and unlike charges attract one another. Thus electrons, which are negatively charged, repel each other but attract protons. Likewise, protons repel each other.



The absolute value of the force F between two point charges q and Q relates to the distance between the point charges and to the simple product of their charges. The diagram shows that like charges repel each other, and opposite charges attract each other. (CC BY-NC; Ümit Kaya)

Each atom is made up of a nucleus in the center, which consists of a number of protons and neutrons, depending upon the element in question. Surrounding the nucleus are electrons that float around the nucleus in what can be thought of as a cloud. As two atoms approach one another, the protons of one atom attract the electrons of the other atom. Similarly, the protons of the other atom attract the electrons of the first atom. As a result, the simultaneous attraction of the components from one atom to another create a bond. This interaction can be summarized mathematically and is known as Coulombic forces:

$$F = k\frac{q_1 q_2}{r^2} \tag{10.2.1}$$

In this mathematical representation of Coulomb's observations,

- F is the electrical force acting between two atoms
- with q_1 and q_2 representing the magnitude of the charges of each atom,
- r is the distance between the two atoms.
- and k is a constant.

From Equation 10.2.1, the electrostatic force between two charges is *inversely* proportional to the *square* of the distance separating the two atoms.

Ion–Ion Interactions

The interactions between ions (ion - ion interactions or charge-charge interactions) are the easiest to understand since such interactions are just a simple application of Coulombic forces (Equation 10.2.1). This specific interaction operates over relatively long distances in the gas phase and is responsible for the attraction of opposite charge ions and the repulsion of like charged ions.

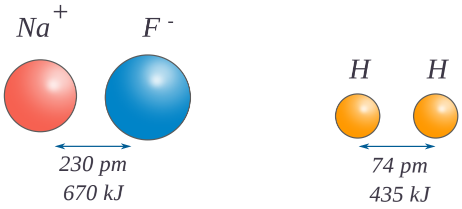


Figure 10.2.1: Ion-Ion attraction in NaF (left) exceeds the covalent bond energy of H_2 (right). (CC BY-NC; Ümit Kaya)

Coulombic forces are also involved in all forms of chemical bonding; when they act between separate charged particles they are especially strong. Thus the energy required to pull a mole of Na^+ and F^- ions apart in the sodium fluoride crystal is greater than that needed to break the a covalent bonds of a mole of H_2. The effects of ion-ion attraction are seen most directly in salts such as NaF and NaCl that consist of oppositely-charged ions arranged in inter-penetrating crystal lattices.

According to Coulomb's Law the force between two charged particles is given by

$$\underbrace{F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2}}_{\text{ion-ion Force}} \tag{10.2.2}$$

Instead of using SI units, chemists often prefer to express atomic-scale distances in picometers and charges as electron charge (±1, ±2, etc.) Using these units, the proportionality constant $1/4\pi\epsilon$ works out to $2.31 \times 10^{16}\ J\ pm$. The sign of F determines whether the force will be attractive (–) or repulsive (+); notice that the latter is the case whenever the two q's have the same sign. Two oppositely-charged particles flying about in a vacuum will be attracted toward each other, and the force becomes stronger and stronger as they approach until eventually they will stick together and a considerable amount of energy will be required to separate them.

Figure 10.2.2: Ion - Ion Interactions in the Gas Phase. (Gary L. Bertrand).

They form an *ion-pair*, a new particle which has a positively-charged area and a negatively-charged area. There are fairly strong interactions between these ion pairs and free ions, so that these clusters tend to grow, and they will eventually fall out of the gas phase as a liquid or solid (depending on the temperature).

> Equation 10.2.2 is an example of an *inverse square law*; the force falls off as the square of the distance. A similar law governs the manner in which the illumination falls off as you move away from a point light source; recall this the next time you walk away from a street light at night, and you will have some feeling for what an inverse square law means.

The stronger the attractive force acting between two particles, the greater the amount of work required to separate them. Work represents a flow of energy, so the foregoing statement is another way of saying that when two particles move in response to a force, their potential energy is lowered. This work is found by integrating the negative of the force function with respect to distance over the distance moved. Thus the energy that must be supplied in order to completely separate two oppositely-charged particles initially at a distance r_0 is given by

$$w = -\int_{r_o}^{\infty} \frac{q_1 q_2}{4\pi\epsilon_0 r^2} dr = -\frac{q_1 q_2}{4\pi\epsilon_0 r_o} \tag{10.2.3}$$

hence, the potential ($V_{ion-ion}$) responsible for the ion-ion force is

$$\underbrace{V_{ion-ion} = \frac{q_1 q_2}{4\pi\epsilon_0 r}}_{\text{ion-ion potential}} \tag{10.2.4}$$

✓ Example 10.2.1

When sodium chloride is melted, some of the ion pairs vaporize and form neutral NaCl dimers. How much energy would be released when one mole of $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions are brought together to generate dimers in this way? The bondlength of NaCl is 237 pm.

Solution

The interactions involved in forming NaCl dimers is the ion-ion forces with a potential energy given by Equation 10.2.4. However, this is the energy of interaction for one pair of $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ion and needs to be scaled by a mole. So the energy released will be

$$\begin{aligned} E &= N_a V(\mathrm{NaCl}) \\ &= N_a \frac{q_1 q_2}{4\pi\epsilon_0 r} \end{aligned}$$

The r in this equation is the distance between the two ions, which is the bondlength of 237 pm ($237 \times 10^{-12} m$).

$$\begin{aligned} E &= (6.022 \times 10^{23}) \underbrace{(8.987 \times 10^9 Nm^2/C^2)}_{1/4\pi\epsilon_o} \frac{(+1.6 \times 10^{-19} C)(-1.6 \times 10^{-19} C)}{237 \times 10^{-12} m} \\ &= -584\ kJ/mol \end{aligned}$$

This is not the energy needed to separate one mole of NaCl since that is a lattice and has more than pairwise interactions and require addressing the geometric orientation of the lattice (see Madelung Constants for more details).

Intermolecular forces are electrostatic in nature; that is, they arise from the electrostatic interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures (i.e., real gases).

Ion-Dipole Interactions

A dipole that is close to a positive or negative ion will orient itself so that the end whose partial charge is opposite to the ion charge will point toward the ion. This kind of interaction is very important in aqueous solutions of ionic substances; H_2O is a highly polar molecule, so that in a solution of sodium chloride, for example, the $\mathrm{Na^+}$ ions will be enveloped by a shell of water molecules with their oxygen-ends pointing toward these ions, while H_2O molecules surrounding the Cl^- ions will have their hydrogen ends directed inward. As a consequence of ion-dipole interactions, all ionic species in aqueous solution are hydrated; this is what is denoted by the suffix in formulas such as $K^+(aq)$, etc.

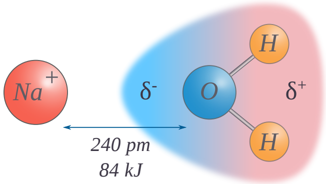


Figure 10.2.3: Ion - Dipole Interaction. (CC BY-NC; Ümit Kaya)

The strength of ion-dipole attraction depends on the magnitude of the dipole moment and on the charge density of the ion. This latter quantity is just the charge of the ion divided by its volume. Owing to their smaller sizes, positive ions tend to have larger charge densities than negative ions, and they should be more strongly hydrated in aqueous solution. The hydrogen ion, being nothing more than a bare proton of extremely small volume, has the highest charge density of any ion; it is for this reason that it exists entirely in its hydrated form H_3O^+ in water.

Since there is now both attractive and repulsive interactions and they both get weaker as the ion and dipole distance increases while also approaching each other in strength, the net ion-dipole is an inverse square relationship as shown in Equation 10.2.5.

$$\underbrace{E \propto \frac{-|q_1|\mu_2}{r^2}}_{\text{ion-dipole potential}} \tag{10.2.5}$$

- r is the distance of separation.
- q is the charge of the ion (only the magnitude of the charge is shown here.)
- μ is the permanent dipole moment of the polar molecule.

$$\vec{\mu} = q'\,\vec{d} \tag{10.2.6}$$

where q' is the partial charge of each end of the dipole and d is the separation between the charges within the dipole

Ion-Ion vs. Ion-Dipole potentials

There are several differences between ion-ion potential (Equation 10.2.4) and the ion-dipole potential (Equation 10.2.5) interactions.

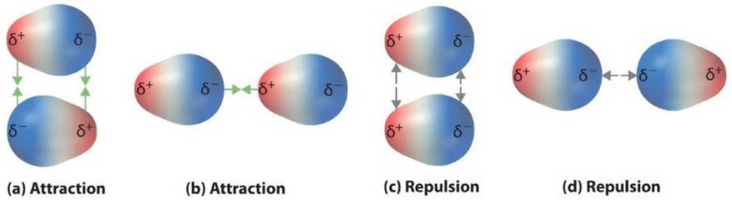
- First, the potential of ion/dipole interactions are negative and net interaction will always be attractive, since the attraction of the opposite dipole to the ion will make it closer than the dipole with the like charge. By using the absolute value of the charge of the ion, and placing a negative sign in front of the equation, this results in a lowering of the potential energy (μ is positive).
- Second, the potential drops off quicker in Equation 10.2.5, where it is an inverse square relationship to the radius ($1/r^2$), while a simple charge-charge interaction (Equation 10.2.4) has a linear inverse relationship ($1/r$). This means the ion-dipole are a shorter range interaction and diminish more rapidly the father the polar molecule is from the ion.
- Third, note that the units of the two equations are the same, as μ has the units of charge X distance. However, the distance in μ is the distance between the dipoles of the polar molecule, while the distance denoted by the "r" is the distance between the ion and the dipole.

It needs to be understood that the molecules in a solution are rotating and vibrating and actual systems are quite complicated (Figure 10.2.4). What is important to realize is that these interactions are Coulombic in nature and how the mathematical equations describe this in terms of the magnitude of the charges and their distances from each other. In this course we will not be calculating dipole moments or the magnitudes of them, but understanding how to read the equations, and developing qualitative understandings that allow us to predict trends.

Figure 10.2.4: Ion-Dipole Interactions in the gas phase. (Gary L. Bertrand).

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in part (a) in Figure 10.2.1.



(a) Attraction (b) Attraction (c) Repulsion (d) Repulsion

Figure 10.2.5: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure 10.2.1c). Hence dipole–dipole interactions, such as those in Figure 10.2.5b, are *attractive intermolecular interactions*, whereas those in Figure 10.2.5d are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 10.2.2. On average, however, the attractive interactions dominate.

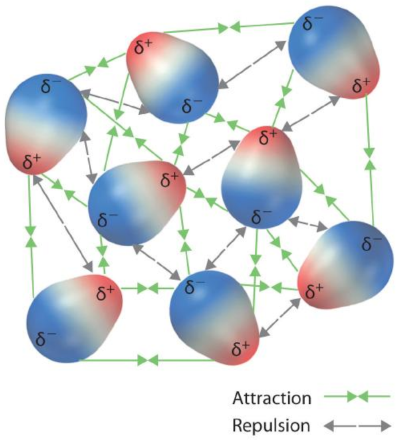


Figure 10.2.6: Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half.

In contrast, the energy of the interaction of two dipoles is proportional to $1/r^6$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^6, or 64-fold:

$$V = -\frac{2\mu_A^2\mu_B^2}{3(4\pi\epsilon_0)^2 r^6}\frac{1}{k_B T} \tag{10.2.7}$$

Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table $10.2.1$. Using what we learned about predicting relative bond polarities from the electronegativities of the bonded atoms, we can make educated guesses about the relative boiling points of similar molecules.

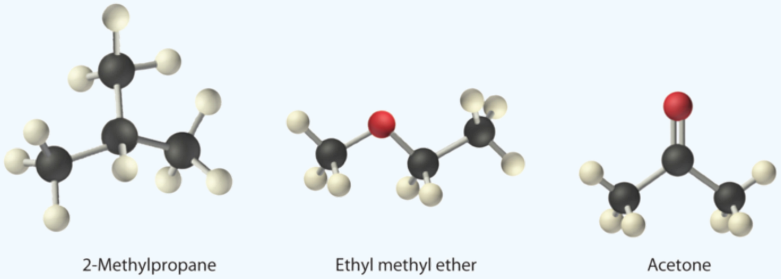
Table 10.2.1: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

> The attractive energy between two ions is proportional to 1/*r*, whereas the attractive energy between two dipoles is proportional to $1/r^6$.

✓ Example $10.2.2$

Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:



Given: compounds

Asked for: order of increasing boiling points

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds. The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point. Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point. Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point. Thus we predict the following order of boiling points: 2-methylpropane < ethyl methyl ether < acetone. This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

? Exercise 10.2.1

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer

dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

London Dispersion Forces

Thus far we have considered only interactions between polar molecules, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 10.2.2).

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table 10.2.2: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 10.2.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.

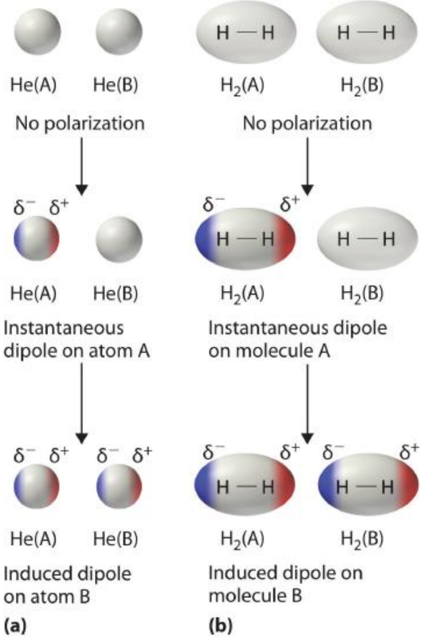


Figure 10.2.3: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure 10.2.3, tends to become more pronounced as atomic and molecular masses increase (Table 10.2.2). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

> *For similar substances, London dispersion forces get stronger with increasing molecular size.*

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 10.2.4). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 10.2.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

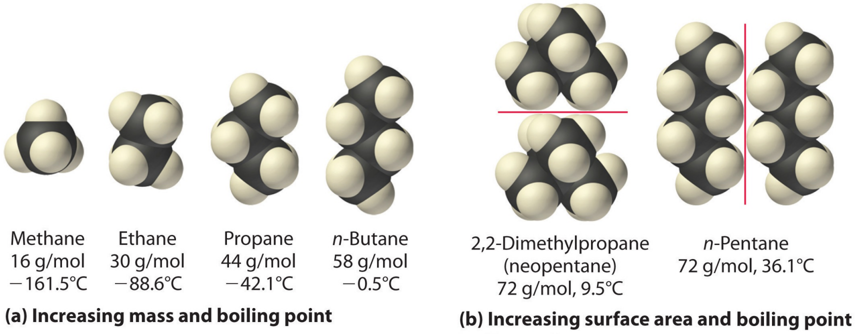


Figure 10.2.4: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

✓ Example 10.2.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

? Exercise 10.2.2

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer

$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed.

10.3: Intermolecular Forces in Liquids

Learning Objectives

- To describe the intermolecular forces in liquids.

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 10.3.1. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

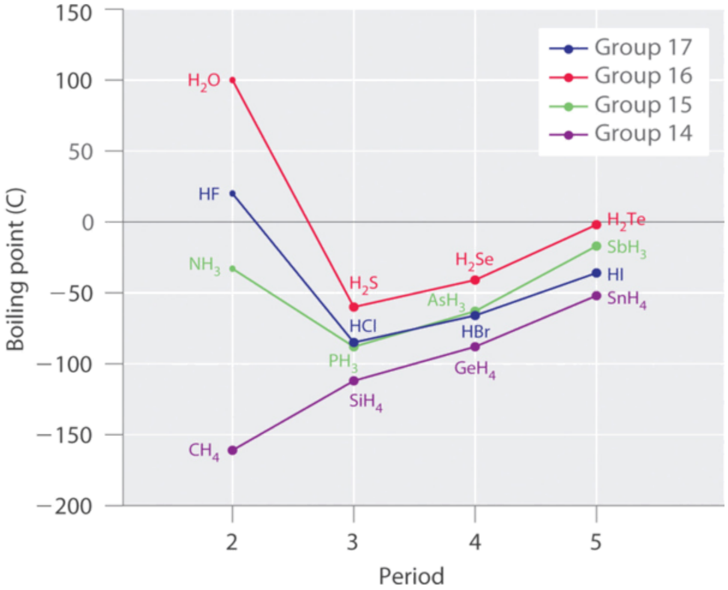


Figure 10.3.1: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure 10.3.2. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O⋯H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

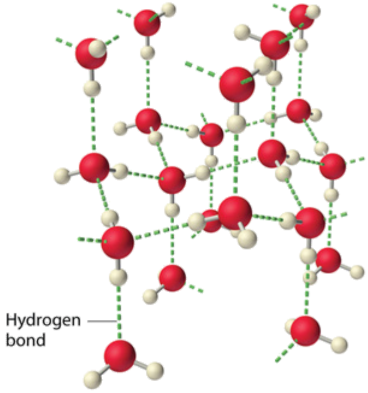


Figure 10.3.2: The Hydrogen-Bonded Structure of Ice

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

It takes two to tango...

Hydrogen bond formation requires *both* a hydrogen bond donor *and* a hydrogen bond acceptor.

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Example 10.3.1

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

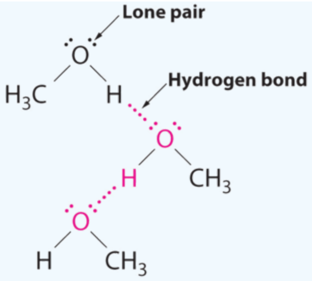
Strategy:

A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.
B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



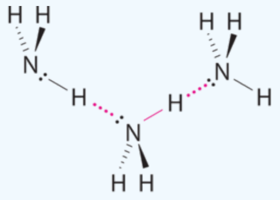
Hydrogen bonding in methanol

Exercise 10.3.1

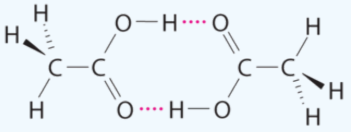
Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

Example 10.3.2

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Spinning Buckminsterfullerene (C_{60}). (CC BY-SA 3.0; unported; Sponk).

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses:

$$\text{He } (-269°\text{C}) < \text{Ar } (-185.7°\text{C}) < N_2O\ (-88.5°\text{C}) < C_{60}\ (>280°\text{C}) < \text{NaCl } (1465°\text{C}).$$

Exercise 10.3.2

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer

$$\text{KBr } (1435°\text{C}) > \text{2,4-dimethylheptane } (132.9°\text{C}) > CS_2\ (46.6°\text{C}) > Cl_2\ (-34.6°\text{C}) > \text{Ne } (-246°\text{C})$$

Special Properties of Water

Besides mercury, water has the highest surface tension for all liquids. Water's high surface tension is due to the hydrogen bonding in water molecules. Water also has an exceptionally high heat of vaporization. Vaporization occurs when a liquid changes to a gas, which makes it an endothermic reaction. Water's heat of vaporization is 41 kJ/mol. Vapor pressure is inversely related to intermolecular forces, so those with stronger intermolecular forces have a lower vapor pressure. Water has very strong intermolecular forces, hence the low vapor pressure, but it's even lower compared to larger molecules with low vapor pressures.

- Viscosity is the property of fluid having high resistance to flow. We normally think of liquids like honey or motor oil being viscous, but when compared to other substances with like structures, water is viscous. Liquids with stronger intermolecular interactions are usually more viscous than liquids with weak intermolecular interactions.
- Cohesion is intermolecular forces between like molecules; this is why water molecules are able to hold themselves together in a drop. Water molecules are very cohesive because of the molecule's polarity. This is why you can fill a glass of water just barely above the rim without it spilling.

Because of water's polarity, it is able to dissolve or dissociate many particles. Oxygen has a slightly negative charge, while the two hydrogens have a slightly positive charge. The slightly negative particles of a compound will be attracted to water's hydrogen atoms, while the slightly positive particles will be attracted to water's oxygen molecule; this causes the compound to dissociate.

Besides the explanations above, we can look to some attributes of a water molecule to provide some more reasons of water's uniqueness:

- Forgetting fluorine, oxygen is the most electronegative non-noble gas element, so while forming a bond, the electrons are pulled towards the oxygen atom rather than the hydrogen. This creates two polar bonds, which make the water molecule more polar than the bonds in the other hydrides in the group.
- A 104.5° bond angle creates a very strong dipole.
- Water has hydrogen bonding which probably is a vital aspect in water's strong intermolecular interaction

Figure 10.3.3: Young boy with father ice fish. The fish do not freeze below the ice surface of the lake due to the unique properties of water. (Public Domain; U.S. Fish and Wildlife Service).

The properties of water make it suitable for organisms to survive in during differing weather conditions. Water expands as it freezes, which explains why ice is able to float on liquid water. During the winter when lakes begin to freeze, the surface of the water freezes and then moves down toward deeper water; this explains why people can ice skate on or fall through a frozen lake. If ice was not able to float, the lake would freeze from the bottom up killing all ecosystems living in the lake. However ice floats, so the fish are able to survive under the surface of the ice during the winter. The surface of ice above a lake also shields lakes from the cold temperature outside and insulates the water beneath it, allowing the lake under the frozen ice to stay liquid and maintain a temperature adequate for the ecosystems living in the lake to survive.

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong $O\cdots H$ hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cagelike structure that is less dense than liquid water.

10.4: Phase Equilibrium

Learning Objectives

- To know how and why the vapor pressure of a liquid varies with temperature.
- To understand that the equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.
- To understand that the relationship between pressure, enthalpy of vaporization, and temperature is given by the Clausius-Clapeyron equation.

Nearly all of us have heated a pan of water with the lid in place and shortly thereafter heard the sounds of the lid rattling and hot water spilling onto the stovetop. When a liquid is heated, its molecules obtain sufficient kinetic energy to overcome the forces holding them in the liquid and they escape into the gaseous phase. By doing so, they generate a population of molecules in the vapor phase above the liquid that produces a pressure—the vapor pressure of the liquid. In the situation we described, enough pressure was generated to move the lid, which allowed the vapor to escape. If the vapor is contained in a sealed vessel, however, such as an unvented flask, and the vapor pressure becomes too high, the flask will explode (as many students have unfortunately discovered). In this section, we describe vapor pressure in more detail and explain how to quantitatively determine the vapor pressure of a liquid.

Evaporation and Condensation

Because the molecules of a liquid are in constant motion, we can plot the fraction of molecules with a given kinetic energy (KE) against their kinetic energy to obtain the kinetic energy distribution of the molecules in the liquid (Figure $10.4.1$), just as we did for a gas. As for gases, increasing the temperature increases both the average kinetic energy of the particles in a liquid and the range of kinetic energy of the individual molecules. If we assume that a minimum amount of energy (E_0) is needed to overcome the intermolecular attractive forces that hold a liquid together, then some fraction of molecules in the liquid always has a kinetic energy greater than E_0. The fraction of molecules with a kinetic energy greater than this minimum value increases with increasing temperature. Any molecule with a kinetic energy greater than E_0 has enough energy to overcome the forces holding it in the liquid and escape into the vapor phase. Before it can do so, however, a molecule must also be at the surface of the liquid, where it is physically possible for it to leave the liquid surface; that is, only molecules at the surface can undergo evaporation (or vaporization), where molecules gain sufficient energy to enter a gaseous state above a liquid's surface, thereby creating a vapor pressure.

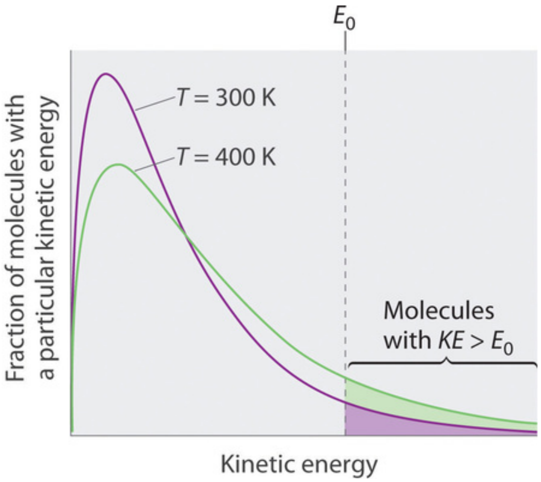


Figure 10.4.1: The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures. Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature. (CC BY-SA-NC; Anonymous by request)

Graph of fraction of molecules with a particular kinetic energy against kinetic energy. Green line is temperature at 400 kelvin, purple line is temperature at 300 kelvin.

To understand the causes of vapor pressure, consider the apparatus shown in Figure 10.4.2. When a liquid is introduced into an evacuated chamber (part (a) in Figure 10.4.2), the initial pressure above the liquid is approximately zero because there are as yet no molecules in the vapor phase. Some molecules at the surface, however, will have sufficient kinetic energy to escape from the liquid and form a vapor, thus increasing the pressure inside the container. As long as the temperature of the liquid is held constant, the fraction of molecules with $KE > E_0$ will not change, and the rate at which molecules escape from the liquid into the vapor phase will depend only on the surface area of the liquid phase.

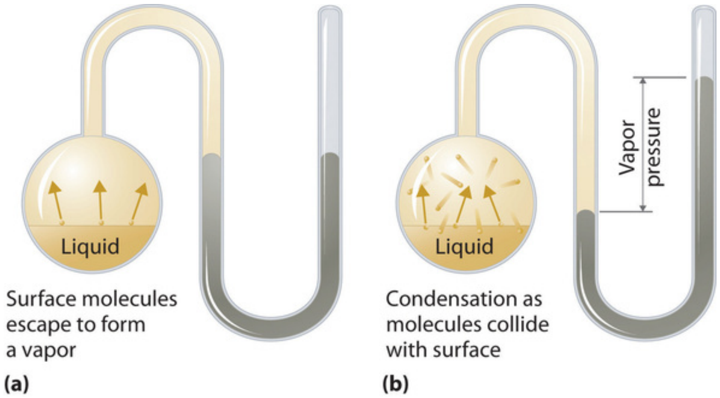


Figure 10.4.2: Vapor Pressure. (a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant. (CC BY-SA-NC; Anonymous by request)

As soon as some vapor has formed, a fraction of the molecules in the vapor phase will collide with the surface of the liquid and reenter the liquid phase in a process known as condensation (part (b) in Figure 10.4.2). As the number of molecules in the vapor phase increases, the number of collisions between vapor-phase molecules and the surface will also increase. Eventually, a *steady state* will be reached in which exactly as many molecules per unit time leave the surface of the liquid (vaporize) as collide with it (condense). At this point, the pressure over the liquid stops increasing and remains constant at a particular value that is characteristic of the liquid at a given temperature. The rates of evaporation and condensation over time for a system such as this are shown graphically in Figure 10.4.3.

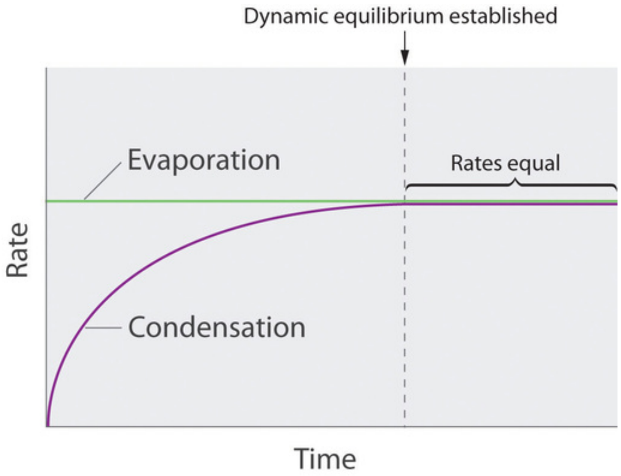


Figure 10.4.3: The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber. The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation. (CC BY-SA-NC; Anonymous by request)

Graph of rate against time. The green line is evaporation while the pruple line is condensation. Dynamic equilibrium is established when the evaporation and condensation rates are equal.

Equilibrium Vapor Pressure

Two opposing processes (such as evaporation and condensation) that occur at the same rate and thus produce no *net* change in a system, constitute a dynamic equilibrium. In the case of a liquid enclosed in a chamber, the molecules continuously evaporate and condense, but the amounts of liquid and vapor do not change with time. The pressure exerted by a vapor in dynamic equilibrium with a liquid is the equilibrium vapor pressure of the liquid.

If a liquid is in an *open* container, however, most of the molecules that escape into the vapor phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and an equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it has "disappeared." The speed with which this occurs depends on the vapor pressure of the liquid and the temperature. Volatile liquids have relatively high vapor pressures and tend to evaporate readily; nonvolatile liquids have low vapor pressures and evaporate more slowly. Although the dividing line between volatile and nonvolatile liquids is not clear-cut, as a general guideline, we can say that substances with vapor pressures greater than that of water (Figure 10.4.4) are relatively volatile, whereas those with vapor pressures less than that of water are relatively nonvolatile. Thus diethyl ether (ethyl ether), acetone, and gasoline are volatile, but mercury, ethylene glycol, and motor oil are nonvolatile.

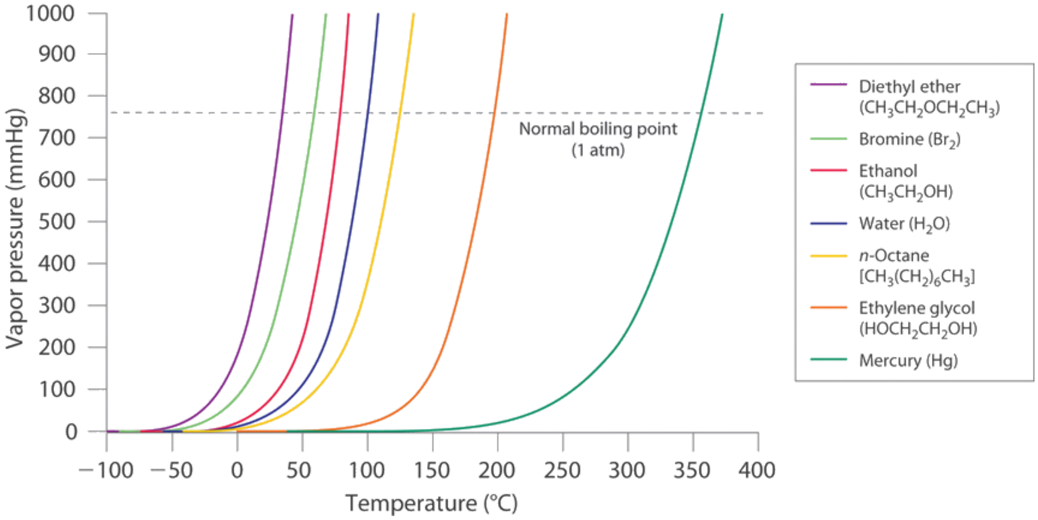


Figure 10.4.4: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the *P* = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC; Anonymous by request)

The equilibrium vapor pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point. It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapor pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure 10.4.4. Molecules that can hydrogen bond, such as ethylene glycol, have a much lower equilibrium vapor pressure than those that cannot, such as octane. The nonlinear increase in vapor pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. The temperature dependence is so strong because the vapor pressure depends on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid, and this fraction increases exponentially with temperature. As a result, sealed containers of volatile liquids are potential bombs if subjected to large increases in temperature. The gas tanks on automobiles are vented, for example, so that a car won't explode when parked in the sun. Similarly, the small cans (1–5 gallons) used to transport gasoline are required by law to have a pop-off pressure release.

> *Volatile substances have low boiling points and relatively weak intermolecular interactions; nonvolatile substances have high boiling points and relatively strong intermolecular interactions.*

A Video Discussing Vapor Pressure and Boiling Points. Video Source: Vapor Pressure & Boiling Point(opens in new window) [youtu.be]

The exponential rise in vapor pressure with increasing temperature in Figure 10.4.4 allows us to use natural logarithms to express the nonlinear relationship as a linear one.

$$\boxed{\ln P = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C} \tag{10.4.1}$$

where

- $\ln P$ is the natural logarithm of the vapor pressure,
- ΔH_{vap} is the enthalpy of vaporization,
- R is the universal gas constant [8.314 J/(mol•K)],
- T is the temperature in kelvins, and
- C is the y-intercept, which is a constant for any given line.

Plotting $\ln P$ versus the inverse of the absolute temperature ($1/T$) is a straight line with a slope of $-\Delta H_{vap}/R$. Equation 10.4.1, called the Clausius–Clapeyron Equation, can be used to calculate the ΔH_{vap} of a liquid from its measured vapor pressure at two or more temperatures. The simplest way to determine ΔH_{vap} is to measure the vapor pressure of a liquid at **two** temperatures and insert the values of P and T for these points into Equation 10.4.2, which is derived from the Clausius–Clapeyron equation:

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{10.4.2}$$

Conversely, if we know ΔH_{vap} and the vapor pressure P_1 at any temperature T_1, we can use Equation 10.4.2 to calculate the vapor pressure P_2 at any other temperature T_2, as shown in Example 10.4.1.

A Video Discussing the Clausius-Clapeyron Equation. Video Link: The Clausius-Clapeyron Equation(opens in new window) [youtu.be]

Example 10.4.1: Vapor Pressure of Mercury

The experimentally measured vapor pressures of liquid Hg at four temperatures are listed in the following table:

experimentally measured vapor pressures of liquid Hg at four temperatures

T (°C)	80.0	100	120	140
P (torr)	0.0888	0.2729	0.7457	1.845

From these data, calculate the enthalpy of vaporization (ΔH_{vap}) of mercury and predict the vapor pressure of the liquid at 160°C. (Safety note: mercury is highly toxic; when it is spilled, its vapor pressure generates hazardous levels of mercury vapor.)

Given: vapor pressures at four temperatures

Asked for: ΔH_{vap} of mercury and vapor pressure at 160°C

Strategy:

A. Use Equation 10.4.2 to obtain ΔH_{vap} directly from two pairs of values in the table, making sure to convert all values to the appropriate units.
B. Substitute the calculated value of ΔH_{vap} into Equation 10.4.2 to obtain the unknown pressure (P_2).

Solution:

A The table gives the measured vapor pressures of liquid Hg for four temperatures. Although one way to proceed would be to plot the data using Equation 10.4.1 and find the value of ΔH_{vap} from the slope of the line, an alternative approach is to use Equation 10.4.2 to obtain ΔH_{vap} directly from two pairs of values listed in the table, assuming no errors in our measurement. We therefore select two sets of values from the table and convert the temperatures from degrees Celsius to kelvin because the equation requires absolute temperatures. Substituting the values measured at 80.0°C (T_1) and 120.0°C (T_2) into Equation 10.4.2 gives

$$\ln\left(\frac{0.7457\ \cancel{Torr}}{0.0888\ \cancel{Torr}}\right) = \frac{-\Delta H_{vap}}{8.314\ J/mol\cdot K}\left(\frac{1}{(120+273)\,K} - \frac{1}{(80.0+273)\,K}\right)$$

$$\ln(8.398) = \frac{-\Delta H_{vap}}{8.314\ J/mol\cdot\ \cancel{K}}\left(-2.88\times 10^{-4}\ \ \cancel{K^{-1}}\right)$$

$$2.13 = -\Delta H_{vap}\left(-3.46\times 10^{-4}\right) J^{-1}\cdot mol$$

$$\Delta H_{vap} = 61,400\ J/mol = 61.4\ kJ/mol$$

B We can now use this value of ΔH_{vap} to calculate the vapor pressure of the liquid (P_2) at 160.0°C (T_2):

$$\ln\left(\frac{P_2}{0.0888\ torr}\right) = \frac{-61,400\ \ J/\cancel{mol}}{8.314\ \ J/\cancel{mol}\ K^{-1}}\left(\frac{1}{(160+273)\,K} - \frac{1}{(80.0+273)\,K}\right)$$

Using the relationship $e^{\ln x} = x$, we have

$$\ln\left(\frac{P_2}{0.0888\ Torr}\right) = 3.86$$

$$\frac{P_2}{0.0888\ Torr} = e^{3.86} = 47.5$$

$$P_2 = 4.21 Torr$$

At 160°C, liquid Hg has a vapor pressure of 4.21 torr, substantially greater than the pressure at 80.0°C, as we would expect.

? Exercise 10.4.1: Vapor Pressure of Nickel

The vapor pressure of liquid nickel at 1606°C is 0.100 torr, whereas at 1805°C, its vapor pressure is 1.000 torr. At what temperature does the liquid have a vapor pressure of 2.500 torr?

Answer

1896°C

Boiling Points

As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point of the liquid. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure 10.4.4 are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm. Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils below 100°C.

Table 10.4.1: The Boiling Points of Water at Various Locations on Earth

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Mt. Everest, Nepal/Tibet	29,028	240	70
Bogota, Colombia	11,490	495	88
Denver, Colorado	5280	633	95
Washington, DC	25	759	100
Dead Sea, Israel/Jordan	−1312	799	101.4

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 mmHg, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 mmHg in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C, respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table 10.4.1 lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a “three-minute egg” may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

> *As pressure increases, the boiling point of a liquid increases and vice versa.*

✓ Example 10.4.2: Boiling Mercury

Use Figure 10.4.4 to estimate the following.

a. the boiling point of water in a pressure cooker operating at 1000 mmHg
b. the pressure required for mercury to boil at 250°C

Mercury boils at 356 °C at room pressure. To see video go to www.youtube.com/watch?v=0iizsbXWYoo

Given: Data in Figure 10.4.4, pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure 10.4.4 and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.
B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

a. **A** The vapor pressure curve of water intersects the P = 1000 mmHg line at about 110°C; this is therefore the boiling point of water at 1000 mmHg.
b. **B** The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx 75$ mmHg. Hence this is the pressure required for mercury to boil at 250°C.

? Exercise 10.4.2: Boiling Ethlyene Glycol

Ethylene glycol is an organic compound primarily used as a raw material in the manufacture of polyester fibers and fabric industry, and polyethylene terephthalate resins (PET) used in bottling. Use the data in Figure 10.4.4 to estimate the following.

a. the normal boiling point of ethylene glycol
b. the pressure required for diethyl ether to boil at 20°C.

Answer a

200°C

Answer b

450 mmHg

Summary

Because the molecules of a liquid are in constant motion and possess a wide range of kinetic energies, at any moment some fraction of them has enough energy to escape from the surface of the liquid to enter the gas or vapor phase. This process, called **vaporization** or **evaporation**, generates a **vapor pressure** above the liquid. Molecules in the gas phase can collide with the liquid surface and reenter the liquid via **condensation**. Eventually, a *steady state* is reached in which the number of molecules evaporating and condensing per unit time is the same, and the system is in a state of **dynamic equilibrium**. Under these conditions, a liquid exhibits a characteristic **equilibrium vapor pressure** that depends only on the temperature. We can express the nonlinear relationship between vapor pressure and temperature as a linear relationship using the **Clausius–Clapeyron equation**. This equation can be used to calculate the enthalpy of vaporization of a liquid from its measured vapor pressure at two or more temperatures. **Volatile liquids** are liquids with high vapor pressures, which tend to evaporate readily from an open container; **nonvolatile liquids** have low vapor pressures. When the vapor pressure equals the external pressure, bubbles of vapor form within the liquid, and it boils. The temperature at which a substance boils at a pressure of 1 atm is its **normal boiling point**.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

10.5: Phase Transitions

Learning Objectives

- To calculate the energy changes that accompany phase changes.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These changes of state are often called phase changes. The six most common phase changes are shown in Figure $10.5.1$.

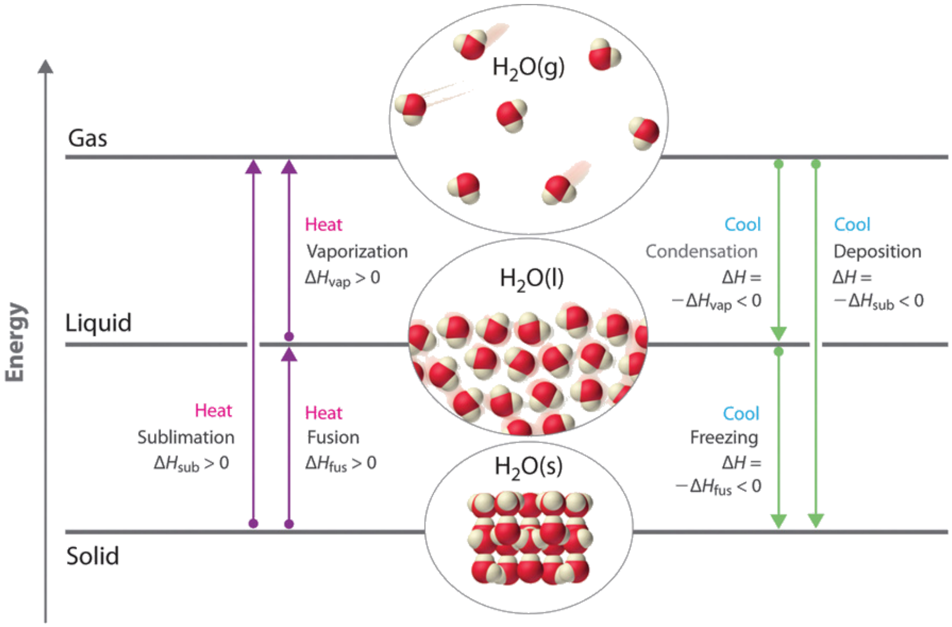


Figure 10.5.1: Enthalpy changes that accompany phase transitions are indicated by purple and green arrows. (CC BY-SA-NC; anoymous)

Purple arrows indicate heatingfrom solid to gas, solid to liquid, and liquid to gas. Green arrows indicate cooling from gas to solid, gas to liquid, and liquid to solid.

Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the energy of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very disordered, have the weakest. Thus any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; it is **endothermic**. Conversely, any transition from a less ordered to a more ordered state (liquid to solid, gas to liquid, or gas to solid) releases energy; it is **exothermic**. The energy change associated with each common phase change is shown in Figure $10.5.1$.

> *ΔH is positive for any transition from a more ordered to a less ordered state and negative for a transition from a less ordered to a more ordered state.*

Previously, we defined the enthalpy changes associated with various chemical and physical processes. The melting points and molar **enthalpies of fusion** (ΔH_{fus}), the energy required to convert from a solid to a liquid, a process known as fusion (or melting), as well as the normal boiling points and enthalpies of vaporization (ΔH_{vap}) of selected compounds are listed in Table $10.5.1$.

Table 10.5.1: Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances. Values given under 1 atm. of external pressure.

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
N_2	−210.0	0.71	−195.8	5.6
HCl	−114.2	2.00	−85.1	16.2
Br_2	−7.2	10.6	58.8	30.0
CCl_4	−22.6	2.56	76.8	29.8
CH_3CH_2OH (ethanol)	−114.1	4.93	78.3	38.6
$CH_3(CH_2)_4CH_3$ (*n*-hexane)	−95.4	13.1	68.7	28.9
H_2O	0	6.01	100	40.7
Na	97.8	2.6	883	97.4
NaF	996	33.4	1704	176.1

The substances with the highest melting points usually have the highest enthalpies of fusion; they tend to be ionic compounds that are held together by very strong electrostatic interactions. Substances with high boiling points are those with strong intermolecular interactions that must be overcome to convert a liquid to a gas, resulting in high enthalpies of vaporization. The enthalpy of vaporization of a given substance is much greater than its enthalpy of fusion because it takes more energy to completely separate molecules (conversion from a liquid to a gas) than to enable them only to move past one another freely (conversion from a solid to a liquid).

> *Less energy is needed to allow molecules to move past each other than to separate them totally.*

Figure 10.5.2: The Sublimation of solid iodine. When solid iodine is heated at ordinary atmospheric pressure, it sublimes. When the I_2 vapor comes in contact with a cold surface, it deposits I_2 crystals. Figure used with permission from Wikipedia.

The direct conversion of a solid to a gas, without an intervening liquid phase, is called sublimation. The amount of energy required to sublime 1 mol of a pure solid is the enthalpy of sublimation (ΔH_{sub}). Common substances that sublime at standard temperature and pressure (STP; 0°C, 1 atm) include CO_2 (dry ice); iodine (Figure $10.5.2$); naphthalene, a substance used to protect woolen clothing against moths; and 1,4-dichlorobenzene. As shown in Figure $10.5.1$, the enthalpy of sublimation of a substance is the sum of its enthalpies of fusion and vaporization provided all values are at the same T; this is an application of Hess's law.

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} \tag{10.5.1}$$

Fusion, vaporization, and sublimation are endothermic processes; they occur only with the absorption of heat. Anyone who has ever stepped out of a swimming pool on a cool, breezy day has felt the heat loss that accompanies the evaporation of water from the skin. Our bodies use this same phenomenon to maintain a constant temperature: we perspire continuously, even when at rest, losing about 600 mL of water daily by evaporation from the skin. We also lose about 400 mL of water as water vapor in the air we exhale, which also contributes to cooling. Refrigerators and air-conditioners operate on a similar principle: heat is absorbed from the object or area to be cooled and used to vaporize a low-boiling-point liquid, such as ammonia or the chlorofluorocarbons (CFCs) and the hydrofluorocarbons (HCFCs). The vapor is then transported to a different location and compressed, thus releasing and dissipating the heat. Likewise, ice cubes efficiently cool a drink not because of their low temperature but because heat is required to convert ice at 0°C to liquid water at 0°C.

Temperature Curves

The processes on the right side of Figure $10.5.1$—freezing, condensation, and deposition, which are the reverse of fusion, sublimation, and vaporization—are exothermic. Thus heat pumps that use refrigerants are essentially air-conditioners running in reverse. Heat from the environment is used to vaporize the refrigerant, which is then condensed to a liquid in coils within a house to provide heat. The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

Heating Curves

Figure $10.5.3$ shows a heating curve, a plot of temperature versus heating time, for a 75 g sample of water. The sample is initially ice at 1 atm and −23°C; as heat is added, the temperature of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s) of ice, which is the number of joules required to raise the temperature of 1 g of ice by 1°C. As the temperature of the ice increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of water is *greater* than that of ice. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

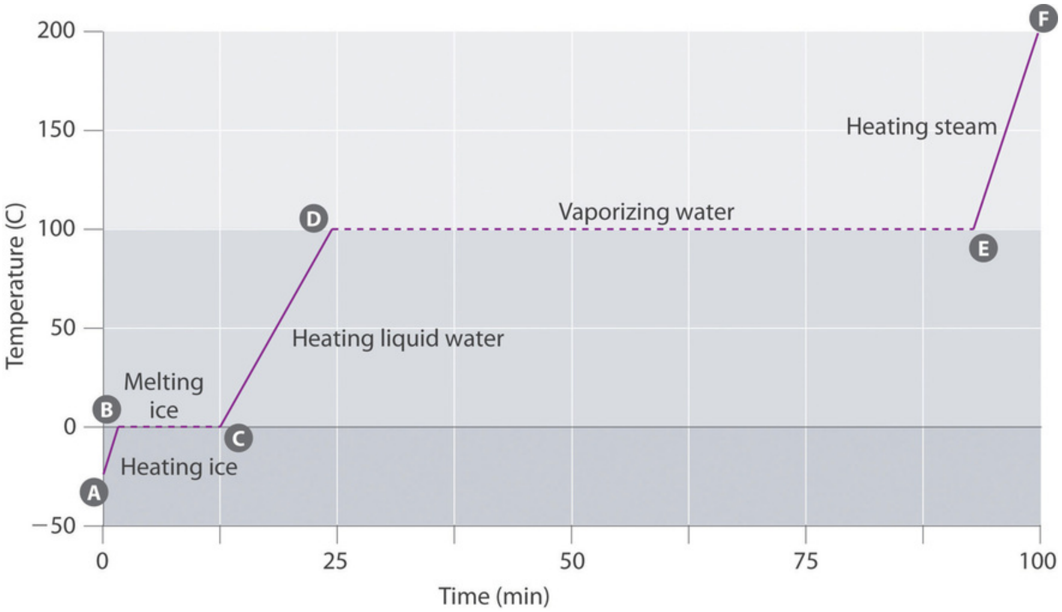


Figure 10.5.3: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and −23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

Thus *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

> *The temperature of a sample does not change during a phase change.*

If heat is added at a constant rate, as in Figure 10.5.3, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure 10.5.3, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquid is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes “bumping” when a liquid is heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or “bump” the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a “boiling chip”) in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The cooling curve, a plot of temperature versus cooling time, in Figure 10.5.4 plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled. Although we might expect the cooling curve to be the mirror image of the heating curve in Figure 10.5.3, the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquid. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystal), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

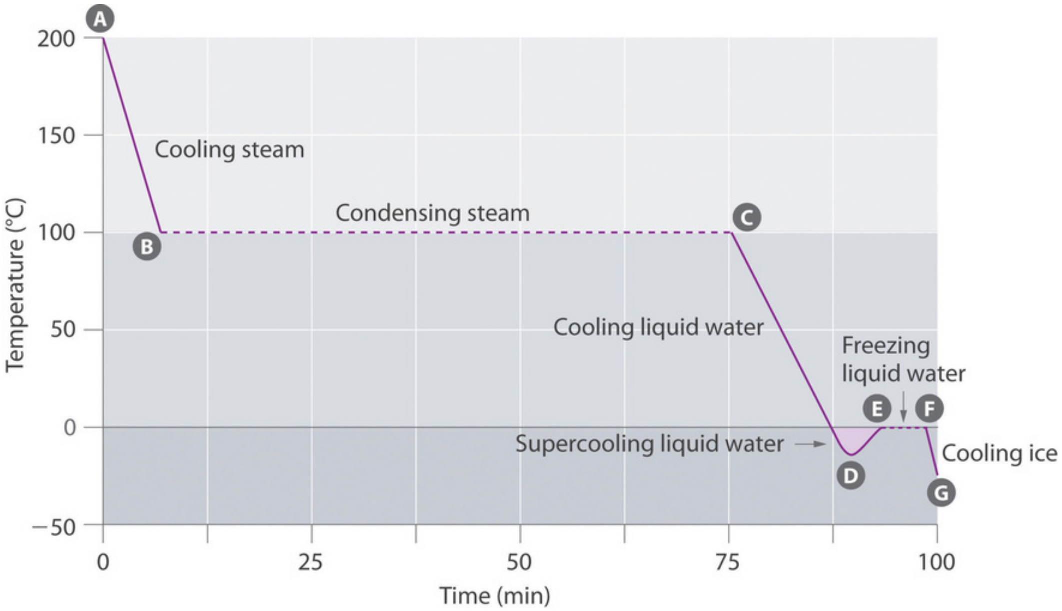


Figure 10.5.4: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth’s climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about −10°C, rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimes, it absorbs heat from the cloud, often with the desired results.

A Video Discussing the Thermodynamics of Phase Changes. Video Source: The Thermodynamics of Phase Changes, YouTube(opens in new window) [youtu.be]

✓ Example 10.5.1: Cooling Tea

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g•°C) and 2.062 J/(g•°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy

Substitute the given values into the general equation relating heat gained (by the ice) to heat lost (by the tea) to obtain the final temperature of the mixture.

Solution

When two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0°C.

The amount of heat gained by the ice cube as it melts is determined by its enthalpy of fusion in kJ/mol:

$$q = n\Delta H_{fus}$$

For our 50.0 g ice cube:

$$\begin{aligned} q_{ice} &= 50.0g \cdot \frac{1\ mol}{18.02\ g} \cdot 6.01\ kJ/mol \\ &= 16.7\ kJ \end{aligned}$$

Thus, when the ice cube has just melted, it has absorbed 16.7 kJ of heat from the tea. We can then substitute this value into the first equation to determine the change in temperature of the tea:

$$q_{tea} = -16,700J = 500mL \cdot \frac{1.00\ g}{1\ mL} \cdot 4.184J/(g\bullet {}^{\circ}C)\Delta T$$

$$\Delta T = -7.98^{\circ}C = T_f - T_i$$

$$T_f = 12.02^{\circ}C$$

This would be the temperature of the tea when the ice cube has just finished melting; however, this leaves the melted ice still at 0.0°C. We might more practically want to know what the final temperature of the mixture of tea will be once the melted ice has come to thermal equilibrium with the tea. To determine this, we can add one more step to the calculation by plugging in to the general equation relating heat gained and heat lost again:

$$\begin{aligned} q_{ice} &= -q_{tea} \\ q_{ice} &= m_{ice} C_s \Delta T = 50.0g \cdot 4.184J/(g\bullet {}^{\circ}C) \cdot (T_f - 0.0^{\circ}C) \\ &= 209.2J/^{\circ}C \cdot T_f \end{aligned}$$

$$q_{tea} = m_{tea} C_s \Delta T = 500g \cdot 4.184J/(g\bullet {}^{\circ}C) \cdot (T_f - 12.02^{\circ}C) = 2092J/^{\circ}C \cdot T_f - 25,150J$$

$$209.2J/^{\circ}C \cdot T_f = -2092J/^{\circ}C \cdot T_f + 25,150J$$

$$2301.2J/^{\circ}C \cdot T_f = 25,150J$$

$$T_f = 10.9^{\circ}C$$

The final temperature is in between the initial temperatures of the tea (12.02 °C) and the melted ice (0.0 °C), so this answer makes sense. In this example, the tea loses much more heat in melting the ice than in mixing with the cold water, showing the importance of accounting for the heat of phase changes!

? Exercise 10.5.1: Death by Freezing

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at −5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you cannot remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at −5.0°C to your body's internal temperature of 37°C. Use the data in Example 10.5.1

Answer

200 kJ (4.1 kJ to bring the ice from −5.0°C to 0.0°C, 133.6 kJ to melt the ice at 0.0°C, and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

Summary

Fusion, vaporization, and sublimation are endothermic processes, whereas freezing, condensation, and deposition are exothermic processes. Changes of state are examples of **phase changes**, or *phase transitions*. All phase changes are accompanied by changes in the energy of a system. Changes from a more-ordered state to a less-ordered state (such as a liquid to a gas) are *endothermic*. Changes from a less-ordered state to a more-ordered state (such as a liquid to a solid) are always *exothermic*. The conversion of a solid to a liquid is called **fusion (or melting)**. The energy required to melt 1 mol of a substance is its enthalpy of fusion (ΔH_{fus}). The energy change required to vaporize 1 mol of a substance is the enthalpy of vaporization (ΔH_{vap}). The direct conversion of a solid to a gas is **sublimation**. The amount of energy needed to sublime 1 mol of a substance is its **enthalpy of sublimation (ΔH_{sub})**

and is the sum of the enthalpies of fusion and vaporization. Plots of the temperature of a substance versus heat added or versus heating time at a constant rate of heating are called **heating curves**. Heating curves relate temperature changes to phase transitions. A **superheated liquid**, a liquid at a temperature and pressure at which it should be a gas, is not stable. A **cooling curve** is not exactly the reverse of the heating curve because many liquids do not freeze at the expected temperature. Instead, they form a **supercooled liquid**, a metastable liquid phase that exists below the normal melting point. Supercooled liquids usually crystallize on standing, or adding a **seed crystal** of the same or another substance can induce crystallization.

10.6: Phase Diagrams

Learning Objectives

- To understand the basics of a one-component phase diagram as a function of temperature and pressure in a closed system.
- To be able to identify the triple point, the critical point, and four regions: solid, liquid, gas, and a supercritical fluid.

The state exhibited by a given sample of matter depends on the identity, temperature, and pressure of the sample. A phase diagram is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system.

Introduction

A typical phase diagram consists of discrete regions that represent the different phases exhibited by a substance (Figure $10.6.1$). Each region corresponds to the range of combinations of temperature and pressure over which that phase is stable. The combination of high pressure and low temperature (upper left of Figure $10.6.1$) corresponds to the solid phase, whereas the gas phase is favored at high temperature and low pressure (lower right). The combination of high temperature and high pressure (upper right) corresponds to a supercritical fluid.

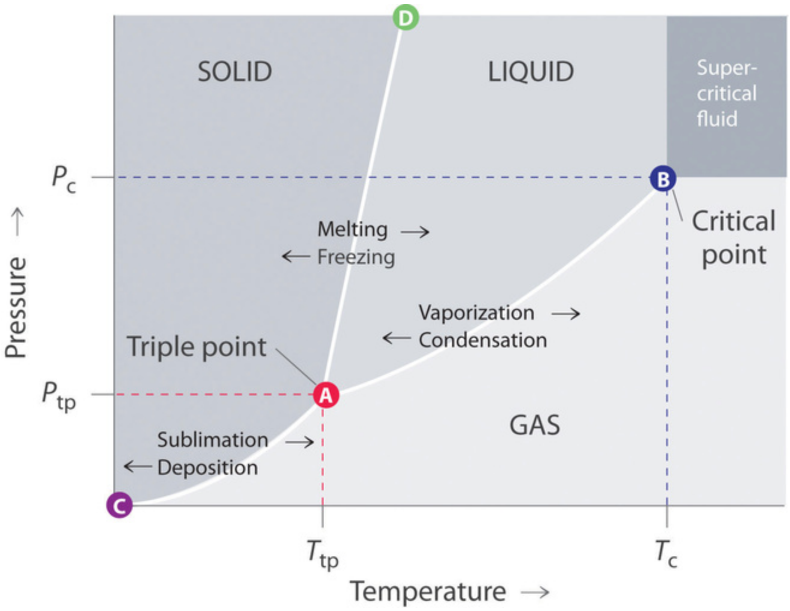


Figure 10.6.1: A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region

> The solid phase is favored at low temperature and high pressure; the gas phase is favored at high temperature and low pressure.

The lines in a phase diagram correspond to the combinations of temperature and pressure at which two phases can coexist in equilibrium. In Figure $10.6.1$, the line that connects points A and D separates the solid and liquid phases and shows how the melting point of a solid varies with pressure. The solid and liquid phases are in equilibrium all along this line; crossing the line horizontally corresponds to melting or freezing. The line that connects points A and B is the vapor pressure curve of the liquid, which we discussed in Section 11.5. It ends at the critical point, beyond which the substance exists as a supercritical fluid. The line that connects points A and C is the vapor pressure curve of the *solid* phase. Along this line, the solid is in equilibrium with the vapor phase through sublimation and deposition. Finally, point A, where the solid/liquid, liquid/gas, and solid/gas lines intersect, is the triple point; it is the *only* combination of temperature and pressure at which all three phases (solid, liquid, and gas) are in equilibrium and can therefore exist simultaneously. Because no more than three phases can ever coexist, a phase diagram can never have more than three lines intersecting at a single point.

Remember that a phase diagram, such as the one in Figure $10.6.1$, is for a single pure substance in a closed system, not for a liquid in an open beaker in contact with air at 1 atm pressure. In practice, however, the conclusions reached about the behavior of a substance in a closed system can usually be extrapolated to an open system without a great deal of error.

The Phase Diagram of Water

Figure $10.6.2$ shows the phase diagram of water and illustrates that the triple point of water occurs at 0.01°C and 0.00604 atm (4.59 mmHg). Far more reproducible than the melting point of ice, which depends on the amount of dissolved air and the atmospheric pressure, the triple point (273.16 K) is used to define the absolute (Kelvin) temperature scale. The triple point also represents the lowest pressure at which a liquid phase can exist in equilibrium with the solid or vapor. At pressures less than 0.00604 atm, therefore, ice does not melt to a liquid as the temperature increases; the solid sublimes directly to water vapor. Sublimation of water at low temperature and pressure can be used to “freeze-dry” foods and beverages. The food or beverage is first cooled to subzero temperatures and placed in a container in which the pressure is maintained below 0.00604 atm. Then, as the temperature is increased, the water sublimes, leaving the dehydrated food (such as that used by backpackers or astronauts) or the powdered beverage (as with freeze-dried coffee).

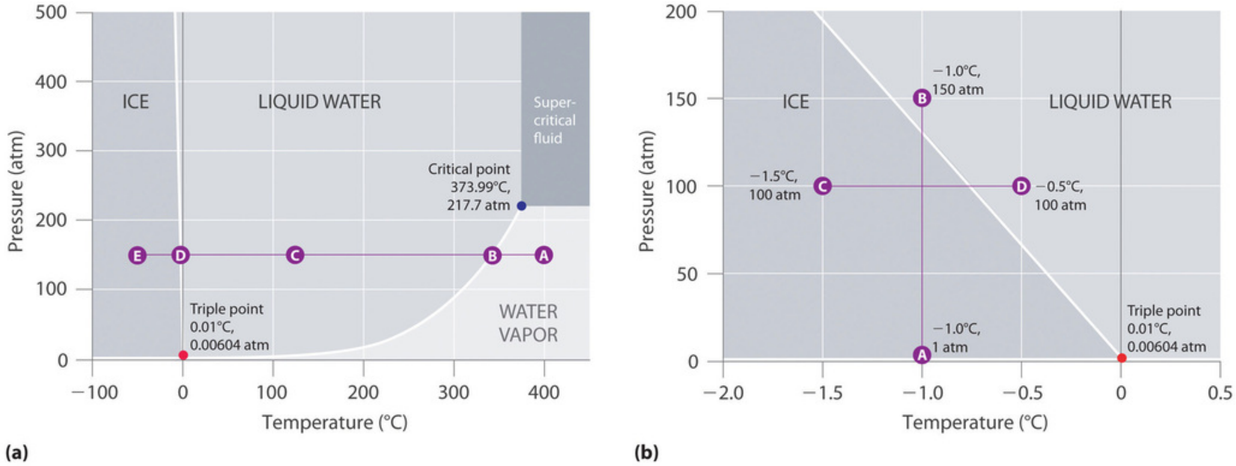


Figure 10.6.2: Two Versions of the Phase Diagram of Water. (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example 10.6.1).

The phase diagram for water illustrated in Figure $10.6.2b$ shows the boundary between ice and water on an expanded scale. The melting curve of ice slopes up and slightly to the left rather than up and to the right as in Figure $10.6.1$; that is, the melting point of ice *decreases* with increasing pressure; at 100 MPa (987 atm), ice melts at −9°C. Water behaves this way because it is one of the few known substances for which the crystalline solid is *less dense* than the liquid (others include antimony and bismuth). Increasing the pressure of ice that is in equilibrium with water at 0°C and 1 atm tends to push some of the molecules closer together, thus decreasing the volume of the sample. The decrease in volume (and corresponding increase in density) is smaller for a solid or a liquid than for a gas, but it is sufficient to melt some of the ice.

In Figure $10.6.2b$ point A is located at P = 1 atm and T = −1.0°C, within the solid (ice) region of the phase diagram. As the pressure increases to 150 atm while the temperature remains the same, the line from point A crosses the ice/water boundary to point B, which lies in the liquid water region. Consequently, applying a pressure of 150 atm will melt ice at −1.0°C. We have already indicated that the pressure dependence of the melting point of water is of vital importance. If the solid/liquid boundary in the phase diagram of water were to slant up and to the right rather than to the left, ice would be denser than water, ice cubes would sink, water pipes would not burst when they freeze, and antifreeze would be unnecessary in automobile engines.

Ice Skating: An Incorrect Hypothesis of Phase Transitions

Until recently, many textbooks described ice skating as being possible because the pressure generated by the skater’s blade is high enough to melt the ice under the blade, thereby creating a lubricating layer of liquid water that enables the blade to slide across the ice. Although this explanation is intuitively satisfying, it is incorrect, as we can show by a simple calculation.

Pressure from ice skates on ice. from wikihow.com.

Recall that pressure (*P*) is the force (*F*) applied per unit area (*A*):

$$P=\frac{F}{A}$$

To calculate the pressure an ice skater exerts on the ice, we need to calculate only the force exerted and the area of the skate blade. If we assume a 75.0 kg (165 lb) skater, then the force exerted by the skater on the ice due to gravity is

$$F=mg$$

where *m* is the mass and *g* is the acceleration due to Earth’s gravity (9.81 m/s^2). Thus the force is

$$F=(75.0\ kg)(9.81\ m/s^2)=736\ (kg\bullet m)/s^2=736N$$

If we assume that the skate blades are 2.0 mm wide and 25 cm long, then the area of the bottom of each blade is

$$A=(2.0\times10^{-3}\ m)(25\times10^{-2}\ m)=5.0\times10^{-4}m^2$$

If the skater is gliding on one foot, the pressure exerted on the ice is

$$P=\frac{736\ N}{5.0\times10^{-4}\ m^2}=1.5\times10^6\ N/m^2=1.5\times10^6\ Pa=15\ atm$$

The pressure is much lower than the pressure needed to decrease the melting point of ice by even 1°C, and experience indicates that it is possible to skate even when the temperature is well below freezing. Thus pressure-induced melting of the ice cannot explain the low friction that enables skaters (and hockey pucks) to glide. Recent research indicates that the surface of ice, where the ordered array of water molecules meets the air, consists of one or more layers of almost liquid water. These layers, together with melting induced by friction as a skater pushes forward, appear to account for both the ease with which a skater glides and the fact that skating becomes more difficult below about −7°C, when the number of lubricating surface water layers decreases.

✓ Example 10.6.1: Water

Referring to the phase diagram of water in Figure $10.6.2$:

a. predict the physical form of a sample of water at 400°C and 150 atm.
b. describe the changes that occur as the sample in part (a) is slowly allowed to cool to −50°C at a constant pressure of 150 atm.

Given: phase diagram, temperature, and pressure

Asked for: physical form and physical changes

Strategy:

A. Identify the region of the phase diagram corresponding to the initial conditions and identify the phase that exists in this region.
B. Draw a line corresponding to the given pressure. Move along that line in the appropriate direction (in this case cooling) and describe the phase changes.

Solution:

a. **A** Locate the starting point on the phase diagram in part (a) in Figure $10.6.2$. The initial conditions correspond to point A, which lies in the region of the phase diagram representing water vapor. Thus water at *T* = 400°C and *P* = 150 atm is a gas.

b. **B** Cooling the sample at constant pressure corresponds to moving left along the horizontal line in part (a) in Figure 10.6.2. At about 340°C (point B), we cross the vapor pressure curve, at which point water vapor will begin to condense and the sample will consist of a mixture of vapor and liquid. When all of the vapor has condensed, the temperature drops further, and we enter the region corresponding to liquid water (indicated by point C). Further cooling brings us to the melting curve, the line that separates the liquid and solid phases at a little below 0°C (point D), at which point the sample will consist of a mixture of liquid and solid water (ice). When all of the water has frozen, cooling the sample to −50°C takes us along the horizontal line to point E, which lies within the region corresponding to solid water. At P = 150 atm and T = −50°C, therefore, the sample is solid ice.

? Exercise 10.6.2

Referring to the phase diagram of water in Figure 10.6.2, predict the physical form of a sample of water at −0.0050°C as the pressure is gradually increased from 1.0 mmHg to 218 atm.

Answer

The sample is initially a gas, condenses to a solid as the pressure increases, and then melts when the pressure is increased further to give a liquid.

The Phase Diagram of Carbon Dioxide

In contrast to the phase diagram of water, the phase diagram of CO_2 (Figure 10.6.3) has a more typical melting curve, sloping up and to the right. The triple point is −56.6°C and 5.11 atm, which means that liquid CO_2 cannot exist at pressures lower than 5.11 atm. At 1 atm, therefore, solid CO_2 sublimes directly to the vapor while maintaining a temperature of −78.5°C, the normal sublimation temperature. Solid CO_2 is generally known as dry ice because it is a cold solid with no liquid phase observed when it is warmed.

Dry ice ($CO_2(s)$) sublimed in air under room temperature and pressure. from Wikipedia.

Also notice the critical point at 30.98°C and 72.79 atm. Supercritical carbon dioxide is emerging as a natural refrigerant, making it a low carbon (and thus a more environmentally friendly) solution for domestic heat pumps.

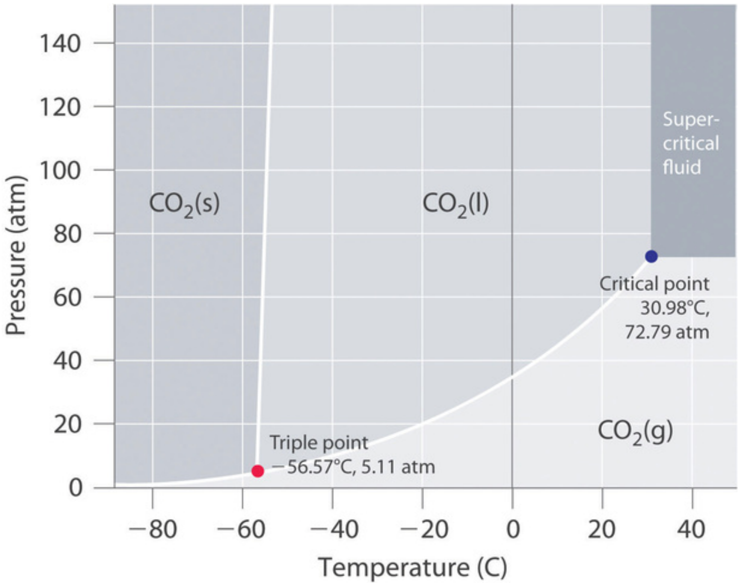


Figure 10.6.3: The Phase Diagram of Carbon Dioxide. Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

The triple point is at -57.57 degrees C and 5.11 atm. The critical point is at 30.98 degree C and 72.79 atm.

The Critical Point

As the phase diagrams above demonstrate, a combination of high pressure and low temperature allows gases to be liquefied. As we increase the temperature of a gas, liquefaction becomes more and more difficult because higher and higher pressures are required to overcome the increased kinetic energy of the molecules. In fact, for every substance, there is some temperature above which the gas can no longer be liquefied, regardless of pressure. This temperature is the critical temperature (T_c), the highest temperature at which a substance can exist as a liquid. Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container. Substances with strong intermolecular forces tend to form a liquid phase over a very large temperature range and therefore have high critical temperatures. Conversely, substances with weak intermolecular interactions have relatively low critical temperatures. Each substance also has a critical pressure (P_c), the minimum pressure needed to liquefy it at the critical temperature. The combination of critical temperature and critical pressure is called the critical point. The critical temperatures and pressures of several common substances are listed in Figure 10.6.1.

Figure 10.6.1: Critical Temperatures and Pressures of Some Simple Substances

Substance	T_c (°C)	P_c (atm)
NH_3	132.4	113.5
CO_2	31.0	73.8
CH_3CH_2OH (ethanol)	240.9	61.4
He	−267.96	2.27
Hg	1477	1587
CH_4	−82.6	46.0
N_2	−146.9	33.9
H_2O	374.0	217.7

> High-boiling-point, nonvolatile liquids have high critical temperatures and vice versa.

Supercritical Fluids

A Video Discussing Phase Diagrams. Video Source: Phase Diagrams(opens in new window) [youtu.be]

10.E: Solids, Liquids, and Phase Transitions (Exercises)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

Q.1

If a substance has relatively strong intermolecular forces, a high melting point, and is not easily compressed, will this substance be a solid, liquid, or gas?

Solution

The substance is a solid because solids have relatively stronger intermolecular forces than liquids or gases. These strong intermolecular forces strongly hold the molecules in the solid together which makes it hard to compress a solid. Solids also have higher melting points because you need to put a lot more energy into solids to break apart the intermolecular forces to make the solid change phases.

Q.3

An unknown sample at 25^oC had a volume of $3.00 \times 10^{14} \mu m^3$ and a mass of $3.20 \times 10^3\ g$.

a. Is this sample most likely in a gaseous state or a condensed one? Why? (HINT: The density of water is $1.000 \frac{g}{mL}$).
b. After completing mass spectroscopy the molar mass of the material was found to be 127 g mol^{-1}, what is the molar volume at 25^oC from using the answer in part (a).

Solution

We need to compute the density of the liquid first:

$$\left(\frac{3.2 \times 10^3 g}{3.0 \times 10^{14}\ \cancel{\mu m^3}}\right)\left(\frac{1.0 \times 10^{12}\ \cancel{\mu m^3}}{1\ \text{cm}^3}\right) = 1.07 \times 10^1 \text{g cm}^{-3}$$

This material is known to be condensed because its density is higher than that of water.

Calculate the molar volume by:

$$\left(\frac{1\ \text{cm}^3}{10.7\ \cancel{g}}\right)\left(\frac{127\ \cancel{g}}{1\ \text{mol}}\right) = 1.19 \times 10^1 \text{cm}^3 mol^{-1}$$

Q.6A

If the volume of a substance changes from 300 cm^3 to 313 cm^3 when it is heated from 25^oC to 40^oC, is the substance ideal gas, nearly ideal gas, or condensed?

Solution

Temperature change = 15^oC

$$\text{Volume change ratio:} \frac{(313-300)}{300} = \frac{13}{300}$$

Hence, change percentage per ^oC is

$$\frac{13}{300} \times \frac{1}{15} \times 100\% = \frac{13}{1500}\% = 0.288\%$$

Since $0.288\%$is close to the ideal gas percentage of 0.366% it is a nearly ideal gas.

Q.6B

Cooling a sample of matter from 130° to 50° at a constant pressure causes its volume to increase from 769.1 to 930.1 cm^3. Classify the material as nearly ideal gas, a non ideal gas, or condensed.

Solution

Charles' Law - Ideal Gases

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$0.00191\frac{L}{K} = 0.00288\frac{L}{K}$$

The material is a non-ideal gas.

Q.7

The molar volume of a substance is the volume occupied by one mole of the substance. The molar volume of a typical solid or liquid is $10\frac{cm^3}{mol}$ to $100\frac{cm^3}{mol}$, while the molar volume of a gas under the same conditions is about $24,000\frac{cm^3}{mol}$. What does the similarity of the molar volumes of solid and liquid forms of the same substance suggest? What does the great difference of the the molar volumes of solid/liquid and gas forms of the same substance suggest?

Solution

The similarity of the molar volumes of solid and liquid forms of the same substance suggests that the distance between neighboring molecules of the substance in solid phase is approximately the same as the distance between neighboring molecules in liquid phase. The great difference of the molar volumes of solid/liquid and gas forms of the same substance suggests that the distance between neighboring molecules of the substance in gas phase is greater the distance between neighboring molecules in solid/liquid phase. This would explain why solids and liquids are called condensed states of matter, because the particles in these two phases are very close together, hence, solids and liquids have definite volumes. While the particles in the gas phase are so far away from each other that they can move freely at high speed, allowing the gas substance to assume the shape and volume of its container.

Q.9

Suppose you have to choose between solid I_2 and solid NH_4Cl to fill your cushion and you prefer softer cushions, which one would you choose and why?

Solution

Non-directional ion-ion interaction is the dominant intermolecular interaction solid NH_4Cl has, and weaker London dispersion forces are the main intermolecular interaction I_2 has, while the feeling of softness (indentation that breaks bonds in the solid) of the two solids depends on their strength of intermolecular interactions; in this case I_2 has weaker intermolecular interactions and will feel softer.

Q.11

The diffusion constant is defined as the amount of substance that when diffusing from a region of high concentration to that of a low concentration goes through each unit of cross section per unit time. What happens to the diffusion constant, at constant temperature, as density of a liquid decreases, as the density of a solid increases, and as the density of a gas decreases? Explain the phenomena.

Solution

As the density of a liquid decreases, the diffusion constant will increase. This is because as density of the liquid decreases, there is more space in between the liquid molecules, and hence more movement is possible for the liquid molecules.

As density of a solid increases, diffusion constant will decrease. Similarly, in concept for the liquid molecules, if the density of a solid increases, there is even less space between the solid molecules than there was before. This further restricts the movements of the solid molecules and decreases diffusion. Note: solids also undergo diffusion; however, it occurs at an extremely slow rate.

As the density of gas decreases, diffusion constant will increase. As the density of a gas decreases, collision between gas molecules will occur less frequently, thus increasing freedom of movement for gas molecules and increasing the diffusion constant.

Q.15

For the following chemicals list attractive intermolecular forces that you expect to see with each chemical. Of the forces you listed for each example, rank the intermolecular forces from strongest to weakest.

a. He
b. $\mathrm{H_2O}$
c. NaCl
d. $\mathrm{CH_4}$
e. CO
f. $\mathrm{O_2}$

Solution

a. London dispersion forces
b. Hydrogen bonding > dispersion forces
c. Ionic bonding > dispersion forces
d. London dispersion forces
e. Dipole-dipole forces > dispersion forces
f. London dispersion forces

Q.17

Which of the the following will be most strongly attracted to a lithium ion:

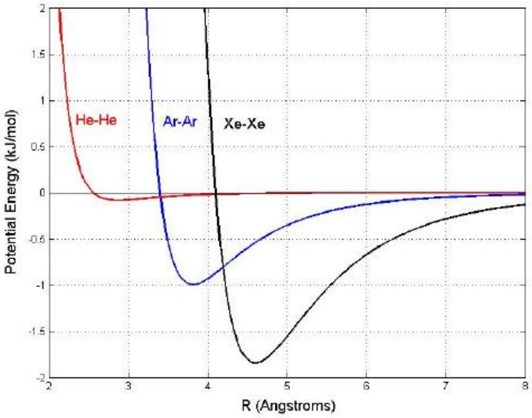
a. fluoride ion
b. a molecule of hydrogen fluoride
c. atom of Argon

Solution

A fluoride ion will be most strongly attracted to a lithium ion. The attraction between unlike charges such as lithium and fluoride are much stronger than the ion dipole attraction between $\mathrm{Li^+}$ and HF and the ion-induced dipole attraction between $\mathrm{Li^+}$ and Ar.

Q.19

Estimate the bond length of $\mathrm{He_2}$, $\mathrm{Ar_2}$, and $\mathrm{Xe_2}$ from the potential energy curves below. For each interacting pair, identify the attractive and repulsive distances. What are the intermolecular forces exist in each of the pair of molecules? Order the potential interactions in term of strength of intermolecular forces.



Solution

- $He_2 \approx 2.7 Å$
- $Ar_2 \approx 3.8 Å$
- $Xe_2 \approx 4.5 Å$

Repulsion is when R less than R at equilibrium. Attraction is when R is bigger than R at equilibrium.

Increasing order of intermolecular forces: $He_2 < Ar_2 < Xe_2$. The intermolecular force that the molecules have is London Dispersion Force (Van der Waals force). Larger molecules tend to have greater polarizability because they have more electrons and their electrons are further away from the nucleus. Therefore, LDF tend to get stronger when the molecule becomes larger. Based on the graph, the higher the potential energy, the stronger the interaction is.

Q.23

Arrange the following substances in order of decreasing normal boiling points and explain the rationale.

a. $CH_3CH_2CH_2CH_2CH_3$
b. $CH_3CH_2CH_2CH_2OH$
c. CH_4
d. $CH_3CH(CH_3)CH_2CH_3$

Solution

$$CH_3CH_2CH_2CH_2OH > CH_3CH_2CH_2CH_2CH_3 > CH_3CH(CH_3)CH_2CH_3 > CH_4$$

1-Butanol has the greatest boiling point due to strong hydrogen bonding with the alcohol group. Pentane has the second strongest boiling point due to its systematical structure and large London Dispersion force. Although 2-methylbutane has the same molecular mass as pentane, its geometrical structure hinders stacking which leads to lower intermolecular force. Therefore, 2-methylbutane has the lowest boiling point.

Q.24

You are given four beakers A, B, C, and D with four different chemicals. You forgot to label the beakers, so to identify them you boiled them to find their normal boiling points. The order of the boiling points came out to be B>D>A>C. If the chemicals in the beakers were HF (Hydrogen Fluoride), Ar (Argon), Cesium Chloride $CsCl$ and Hydrochloric Acid HCl, assign the chemicals to their respective beakers and give the reasoning behind your answer.

Solution

The primary intermolecular forces in the compounds are

- $HF \rightarrow$ Hydrogen Bonding
- $Ar \rightarrow$ Dispersion Forces
- $CsCl \rightarrow$ Ionic Bonding
- $HCl \rightarrow$ Dipole-Dipole Interactions

$$\text{Ionic Bonding} > \text{Hydrogen Bonding} > \text{Dipole-Dipole Interactions} > \text{Dispersion Forces}$$

The stronger the intermolecular forces, the lower the vapor pressure, hence the boiling point would be higher.

Hence the beakers contain

- A = HCl
- B = $CsCl$
- C = Ar
- D = HF

Q.25

Like a normal human being, Kris enjoys breathing. But unfortunately for Kris, she is clinically paranoid, and feels as though she's breathing in a little too much ethanol. To calm Kris down, you say that as a vapor, ethanol exists, to an extent, as a dimer, ($(CH_3CH_2OH)_2$), in which two CH_3CH_2OH molecules are held together by hydrogen bonds. Propose and draw a reasonable structure for this dimer to help Kris deal with her problems.

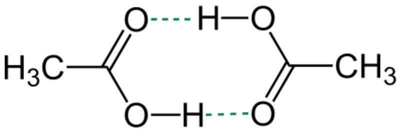
Solution

Hydrogen bonds are a type of intermolecular forces. It is the bond between a hydrogen atom and a high electronegative atom such as N, O, and F. The only hydrogen bonding which can take place between the ethanol molecules is between one's oxygen and the other's hydrogen bonded onto the other's oxygen. So any two membered structure of two ethanol molecukes with this criteria indicated is acceptable.

Q.25

Acetic acid (CH_3COOH) forms a dimer in the gas phase, where two acetic acid molecules are held together by hydrogen bonds. Draw a reasonable structure for this dimer.

Solution

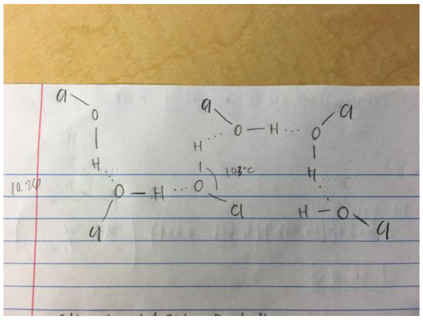


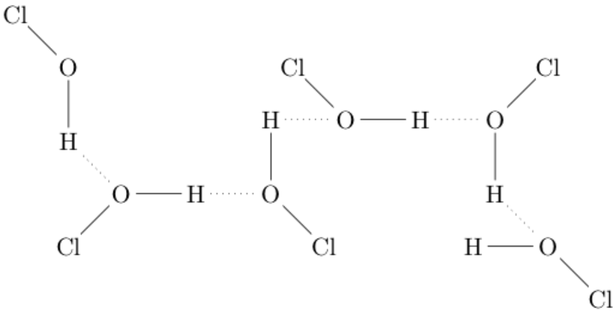
The diagram above shows a reasonable structure of a acetic acid dimer, where the dash lines represent hydrogen bonds.

Q.26

Hypochlorous acid ($HOCl$) is a similar compound to HOF, which is the simplest possible compound that allows comparison between fluoride and oxygen in their abilities to form hydrogen bonds. Although Cl attracts electrons more strongly than O, solid $HOCl$ cannot form $H-Cl$ bonds. Draw the proposed structure for chains of $HOCl$ molecules in the crystalline state. The bond angle for $HOCl$ is 103^o.

Solution





Q.27

How do the boiling points of hydrogen halides differ from that of hydrogen fluoride (HF). Explain your reasoning. Answer: HF has a much higher boiling point (20^oC) compared to the other hydrogen halides. This is because HF is capable of forming hydrogen bonding within its compounds.

Solution

Fluorine is capable of doing hydrogen bonding as opposed to the other halogens in the periodic table. Since fluorine is the element with the highest electronegativity, the hydrogen-fluorine bond in hydrogen fluoride is highly polarized, creating a partial positive charge (δ+) on the hydrogen and, a negative charge (δ-) on the fluorine atom. Furthermore, the lone pairs situated on the fluorine atom are in the second energy level, thus they are very close and the negative charge on the atom is very concentrated, thus it has a strong attraction force. Hydrogen bonds form between the positively charged H atoms and the lone pair of the F atom. The other halogens are not capable of hydrogen bonding because they are not as electronegative as fluorine and they are larger in size. Thus the bond within the molecule is not as polarized and the lone pairs on the halogen atom are not as concentrated. Thus, the stronger the intermolecular forcers of the liquid, the harder it is for a molecule to gain enough energy to overcome the intermolecular forces that bond it in a liquid. The more energy is required to enter the gas phase. The higher the boiling point. Fluorine has higher intermolecular forces, thus it has a higher boiling point compared to the other hydrogen halides.

Q.31

Oxygen is stored at a temperature of 105 K and a pressure of 3.356 atm. If the volume of the container is 2.5 L, calculate the number of moles of oxygen in the container. Compare this number of moles to the number of moles in the same container at standard pressure and 298 K. Is it fewer, more, or unchanged?

Solution

This is an ideal gas law problem, so the formula $PV = nRT$ should be used.

$$P = 3.356\,\text{atm} \quad V = 2.5\,\text{L} \quad n = ? \quad R = 0.0821\frac{\text{L atm}}{\text{mol K}} \quad T = 105K$$

$$n = \frac{3.356 \times 2.5}{0.0821 \times 105}\,\text{mol}$$

$$n = 0.9733\,\text{mol}$$

Standard pressure = 1 atm

$$n = \frac{1 \times 2.5}{0.0821 \times 298}$$

$$n = 0.102\,\text{mol} < 0.9733\,\text{mol}$$

Therefore, under standard conditions, there are fewer moles of oxygen in the container.

Q.35

Consider the reaction at 25ºC.

$$\text{CaC}_2(\text{s}) + 2\,\text{H}_2\text{O}(\text{l}) \longrightarrow \text{C}_2\text{H}_2(\text{g}) + \text{Ca(OH)}_2(\text{s})$$

If the total pressure is 0.9124 atm and the vapor pressure of water at this temperature is 0.0313 atm. What is the mass of acetylene (C_2H_2) per liter of "wet" acetylene collected by this reaction (i.e., collected over a pool of water)? Assume all gases behave ideally.

Solution

Partial pressures in gases are additive via Dalton's Law.

- $P_T = 0.9124 atm$
- $P_{\text{H}_2\text{O}} = 0.0313 atm$

$$P_T - P_{\text{H}_2\text{O}} = P_{\text{C}_2\text{H}_2} = 0.8811 atm$$

Using the Ideal Gas Law, moles per liter of acetylene can be found by rearranging the equation:

$$\frac{n}{V} = \frac{P_{\text{C}_2\text{H}_2}}{RT}$$

$$\frac{0.8811}{0.082057 \times 298.15} = \frac{0.036 mol}{1 L}$$

The question asks for grams per liter, so:

$$\left(\frac{0.036\ \cancel{mol\ C_2H_2}}{1L}\right)\left(\frac{26.036\ gC_2H_2}{1\ \cancel{mol\ C_2H_2}}\right)=0.9376\ \frac{g}{L}$$

Q.39

The highest value of sea-level pressure on Earth occurs in Siberia where the Siberian High often allows water to boil at 80^{o}C. Using chart 10.16 on page 431 of the text book, what can the fraction of pressure be in this location?

Solution

According to the graph, a location where the boiling temperature is 80^{o}C correlates approximately to a fraction of 0.5 atm pressure.

Q.41

Water ($\mathrm{H_2O}$) has a melting point of $0.00\,^\circ\mathrm{C}$ and a boiling point of $100.0\,^\circ\mathrm{C}$. Benzene ($\mathrm{C_6H_6}$) has a melting point of $5.5\,^\circ\mathrm{C}$ and a boiling point of $80.1\,^\circ\mathrm{C}$. At $20.0\,^\circ\mathrm{C}$, which of the two substances would be expected to have a greater surface tension? Explain?

Solution

At $20.0\,^\circ\mathrm{C}$, water $\mathrm{H_2O}$ has a greater surface tension $(72.86\frac{mN}{m})$ than benzene, $(\mathrm{C_6H_6})$, $(28.88\frac{mN}{m})$ because the intermolecular forces between water molecules are stronger than the intermolecular forces between benzene molecules. Water is capable of forming hydrogen-bonds, whereas the only forces that act in benzene are London dispersion forces.

Surface tension is the energy/work required to increase the surface area of a liquid. Molecules at the surface of a liquid do not experience any intermolecular interactions on one interface with air and therefore experience a net attractive force towards the center of the liquid. For surface molecules, the stronger the intermolecular forces between the molecules of the liquid, the stronger the net attractive force towards the center of the liquid will be. Compared to benzene, water possesses stronger intermolecular forces, therefore its surface molecules exhibit a stronger net attractive force towards the center of the liquid. As a result, more energy/work is required to counteract the net attractive force in order to increase the surface area. This indicates that for any liquid, stronger intermolecular forces allow for stronger surface tensions.

Q.43

At gallium's melting point of $302.91K$, its density is $6.095\frac{g}{cm^3}$. The density of solid gallium under standard conditions is $5.91\frac{g}{cm^3}$. When Ga is at $301.91K$ and pressure is strongly increased, will Ga undergo a phase change?

Solution

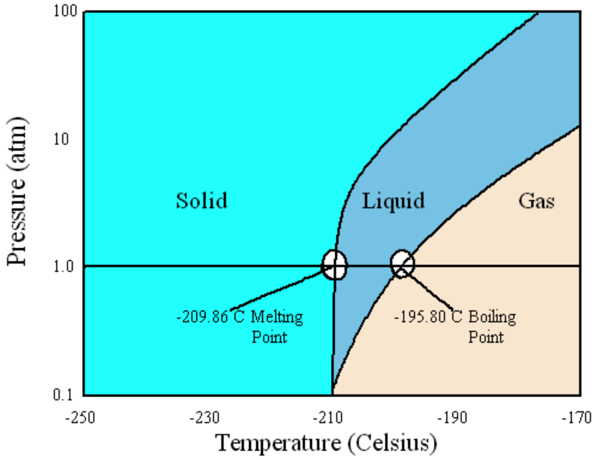
Compression favors the denser phase. Since Ga is a solid at $301.9K$, then it will undergo a phase change to become a liquid.

Q.45

Given the information below, sketch the phase diagram of Nitrogen:

- Triple point: 0.1252 bar, -210°C
- Normal boiling point: 1 bar, -195.8°C
- Normal melting point: 1 bar, -210°C

Solution



Normally, phase diagrams show pressures below that of the critical point.

Q.47

Use the phase diagram of water to determine whether water is a solid, a liquid, or a gas at each of the following combinations of temperature and pressure.

a. 1 atm and 20^oC
b. 0.006 atm and 100^oC
c. 210 atm and 100^oC
d. 10 atm and 50^oC

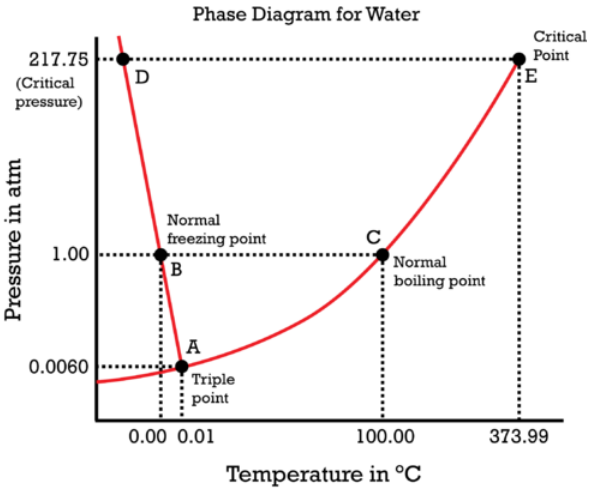


Figure used with permission (CK-12 Foundation – Christopher Auyeung)

Solution

Using the phase diagram of water,

1. Liquid
2. Gaseous
3. Liquid
4. Liquid

Q.53

What phase does candle wax exist in? How about butter?

Solution

Matter can exist in different phases depending on the temperature of the substance. For example, candle wax and butter can exist as a solid at room temperature, but when enough heat is applied to these substances, they can exist in a liquid or a gaseous phase.

Q.59

The equilibrium vapor pressure of water at 19^oC is $0.02168\,atm$ A humidifier is placed in a room with a volume of $180m^3$ and operates until the the room becomes saturated with water vapor. Initially there is no water vapor in water vapor in the air. Assuming that the room is closed completely from the outside such that water vapor cannot escape, calculate the mass of water that has passed into the air.

Solution

The air in the room becomes saturated once the vapor pressure of water in the room is equivalent to the equilibrium vapor pressure of water. Plug in given values into the ideal gas law to find the number of moles of water in the room when it is saturated, and then convert to grams.

$$PV = nRT$$

$$(0.02168atm)(180m^3)(\frac{1000L}{m^3}) = (n)(0.08206\frac{L\,atm}{mol\,K})(292.15K)$$

$$n = 162.77mols$$

$$m = 162.77mols \times \frac{18.02g}{mol} = 2930g$$

Q.65

A cooling bath is a mixture that is primarily liquid which is kept at a constant, low temperature. While in the lab, Po'lah accidently severed its hand after trying to make some mac and cheese. As a result it had to immediately transfer its hand to a cooling bath to sufficiently preserve it but not so that it could be of some use later on. In order to achieve this, the cooling bath had to be kept at around $0^\circ C$. The only liquids it had access to were water and methanol, both at room temperature, and the only cooling agents that it had were liquid nitrogen and dry ice (solid carbon dioxide). What combination did Po'lah use and why?

Relevant Information:

- Carbon Dioxide: sublimes at $-78.5^\circ C$
- Nitrogen: boils at $-195.8^\circ C$
- Water: freezes at $0^\circ C$
- Ethanol: freezes at $-143.7^\circ C$

Solution

This question is a bit tricky. The coolants Liquid Nitrogen and Dry ice, ($\text{CO}_2(\text{s})$), both turn into gasses at very low temperatures. After they turn into gaseous, they are no longer "useful", since they cannot be added into the bath. Therefore, after adding sufficient amounts of either of the coolants to either of the liquids, the temperature of the bath would decrease way past the freezing point of either liquid, resulting in a cooling "block" rather than a bath. So what is the deal? Is this problem unsolvable?

Fortunately, it isn't. Think about a glass of ice water. If enough ice is put into the water, then eventually the water and ice would equilibrate at $0^\circ C$ which is the equilibrium point of the water where both its solid and liquid states can exit. Unfortunately, while the ice is not available at this time, the same concept can be applied. Remember, if enough of either coolant is used, then the entire cup of water will freeze over. However, if just enough of either coolant is put in so that the cooling bath remains at $0^\circ C$, a cooling bath that is somewhat solid and somewhat liquid will form, giving an adequate place for Po'lah to put its hand. Water is perfect for this because it remains a liquid at $0^\circ C$, and cannot exist as such at any lower temperature. Since Ethanol freezes at $-143.7^\circ C$, adding dry ice or liquid nitrogen would bring the cooling bath much lower than $0^\circ C$, which would destroy Po'lah's hand

Thus, it doesn't matter what cooling agent is used, either can bring water down to $0^\circ C$. However, methane cannot be used.

Abstract: Add a little of either coolant to bring the water down to $0^{\circ} C$, and it will remain at both a liquid and a solid which creates a $0^{\circ} C$ cooling bath. Methanol cannot be used.

Q.71

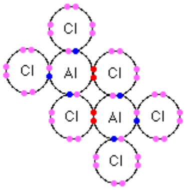
The melting points of the chlorides of third period elements are: $\mathrm{NaCl} = 1074\, K$, $\mathrm{MgCl_2} = 987\, K$, $\mathrm{AlCl_3} = 465\, K$, $\mathrm{SiCl_4} = 204.4\, K$, $\mathrm{PCl_3} = 179\, K$. Based on the applicable intermolecular forces present in each compound, explain this trend in melting points.

Solution

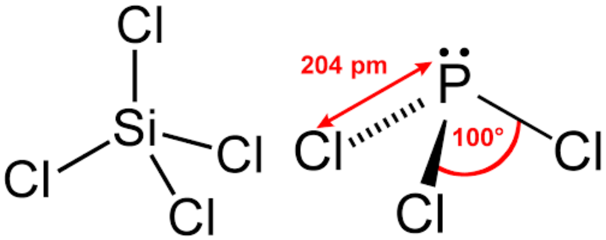
Experimentally, as the chloride compounds make their way across the third period elements, the melting points gradually decrease. This may appear an easy question to address since the melting points are a also measure of the magnitude of the intermolecular forces as play in the specific system, however it a quite complicated and to answer properly require knowledge of the chloride compounds.

Both (NaCl and $\mathrm{MgCl_2}$) are both "ionic solids" with strong ion-ion bonding and hence have the highest melting temperatures in the comparative series. We would expect the $\mathrm{Na^+}$ ions in (NaCl to have weaker Coulombic interactions than the $\mathrm{Mg^{2+}}$ ions in $\mathrm{MgCl_2}$ since the latter are smaller and double the charge (i.e., a higher charge density). That would make the lattice energy higher because it would generate stronger ionic bonds (lattice energy of NaCl and $\mathrm{MgCl_2}$ are 876 and 2526 kJ/mol). However, this ionic perspective is insufficient to explain the observed melting points with ($\mathrm{NaCl} > \mathrm{MgCl_2}$), which we ascribe to bonding never being 100% ionic. As expected for teh difference in electronegativity of chlorine, magnesium, and sodium, the percent ionic character of the $\mathrm{Na-Cl}$ bond is 71% and for $\mathrm{Mg-Cl}$ is even lower, at 58%. Hence, the $\mathrm{Na-Cl}$ bond is 29% covalent and the $\mathrm{Mg-Cl}$ bond is 42% covalent. The covalent character reduces the melting point of $\mathrm{MgCl_2}$, even though $\mathrm{Mg^+}$ has a higher charge-to-size ratio than $\mathrm{Na^+}$.

$\mathrm{AlCl_3}$ is a molecular framework solid which means the solid is an extended covalent molecule and not individual $\mathrm{AlCl_3}$ molecules bound by intermolecular forces.



Both $\mathrm{SiCl_4}$ and $\mathrm{PCl_4}$ solids are molecular in nature. To understand the strength of intermolecular forces as play this properly, we need to apply basic VESPR rules to identify the structures of these molecules.



$\mathrm{SiCl_4}$ is a tetrahedral molecule with no dipole moment (nor quadrupole moment either). $\mathrm{PCl_4}$ is trigonal pyramidal and since P has a different electronegativity than Cl, it has a dipole moment (0.97D). From this argument, we would think that $\mathrm{PCl_4}$ would have a higher melting point, however both molecules have dispersive forces (London) too. Since the magnitude of dispersive forces increased wtih larger molecules (with more electrons to shift around), this is higher in $\mathrm{PCl_4}$, which beats out the weak dipole-dipole interactions in $\mathrm{PCl_4}$.

Q.71

Why are the melting points of NaCl (801 °C) and $\mathrm{MgCl_2}$ (714 °C) so much higher than the melting points of $\mathrm{SCl_2}$ (-122 °C) and $\mathrm{Cl_2}$ (-101.5 °C)? Explain answer in terms of intermolecular forces and identify any potential forces involved.

Solution

As with all bulk properties, the melting points are a measure of the magnitude of the intermolecular forces as play in the specific system (geometric structures also affects bulk properties like the nature of the crystal lattice, but that is a secondary issue). From inspection, it is clear that the $NaCl$ and $MgCl_2$ are ionic held together the strongest permanent electrostatic interaction (charge-charge or monopole-monopole); these are ionic solids. For SCl_2 and Cl_2, the solid is a molecular solid wtih constituent molecules that lack charge and even dipole (easy to tell for Cl_2 and requires a little VSEPR effort for SCl_2. Hence, the next higher permanent electrostatic interactions are active in these molecules (i.e. quadrupole-quadrupole) along with dispersion and repulsive interactions; all of which are much weaker than the charge-charge interactions in $NaCl$ and $MgCl_2$. The weaker the interactions, the lower the boiling point since less thermal energy is needed to break those interactions.

Now, a more advanced question is to explain the origin of the differences in the melting points of $NaCl$ vs. $MgCl_2$. Also to explain the origin of the differences in the melting points of SCl_2 vs. Cl_2. No answer given.

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CHAPTER OVERVIEW

11: Solutions

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

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XVII XVIII XIX XX XXI XXII XXIII ● **Homework Exercises**

Template:HideTOC

A solution is a **homogeneous** mixture composed of two or more substances. In such a mixture, a solute is a substance dissolved in another substance, known as a solvent.

11.1: Composition of Solutions

Learning Objectives

- To describe the concentration of a solution in the way that is most appropriate for a particular problem or application.
- To be familiar with the different units used to express the concentrations of a solution.

There are several different ways to quantitatively describe the concentration of a solution. For example, molarity is a useful way to describe solution concentrations for reactions that are carried out in solution. Mole fractions are used not only to describe gas concentrations but also to determine the vapor pressures of mixtures of similar liquids. Example 11.1.1 reviews the methods for calculating the molarity and mole fraction of a solution when the masses of its components are known.

Example 11.1.1: Molarity and Mole Fraction

Commercial vinegar is essentially a solution of acetic acid in water. A bottle of vinegar has 3.78 g of acetic acid per 100.0 g of solution. Assume that the density of the solution is 1.00 g/mL.

a. What is its molarity?
b. What is its mole fraction?

Given: mass of substance and mass and density of solution

Asked for: molarity and mole fraction

Strategy:

A. Calculate the number of moles of acetic acid in the sample. Then calculate the number of liters of solution from its mass and density. Use these results to determine the molarity of the solution.
B. Determine the mass of the water in the sample and calculate the number of moles of water. Then determine the mole fraction of acetic acid by dividing the number of moles of acetic acid by the total number of moles of substances in the sample.

Solution:

A: The molarity is the number of moles of acetic acid per liter of solution. We can calculate the number of moles of acetic acid as its mass divided by its molar mass.

$$\begin{aligned}\text{moles } \mathrm{CH_3CO_2H} &= \frac{3.78 \ \cancel{\mathrm{g}}\ \mathrm{CH_3CO_2H}}{60.05 \ \cancel{\mathrm{g}}/\mathrm{mol}} \\ &= 0.0629 \text{ mol}\end{aligned}$$

The volume of the solution equals its mass divided by its density.

$$\begin{aligned}\text{volume} &= \frac{\text{mass}}{\text{density}} \\ &= \frac{100.0 \ \cancel{\mathrm{g}}\ \text{solution}}{1.00 \ \cancel{\mathrm{g}}/\mathrm{mL}} = 100 \ mL\end{aligned}$$

Then calculate the molarity directly.

$$\begin{aligned}\text{molarity of } \mathrm{CH_3CO_2H} &= \frac{\text{moles } \mathrm{CH_3CO_2H}}{\text{liter solution}} \\ &= \frac{0.0629 \ mol \ \mathrm{CH_3CO_2H}}{(100 \ \cancel{\mathrm{mL}})(1 \ L/1000 \ \cancel{\mathrm{mL}})} = 0.629 \ M \ \mathrm{CH_3CO_2H}\end{aligned}$$

This result makes intuitive sense. If 100.0 g of aqueous solution (equal to 100 mL) contains 3.78 g of acetic acid, then 1 L of solution will contain 37.8 g of acetic acid, which is a little more than $\frac{1}{2}$ mole. Keep in mind, though, that the mass and volume of a solution are related by its density; concentrated aqueous solutions often have densities greater than 1.00 g/mL.

B: To calculate the mole fraction of acetic acid in the solution, we need to know the number of moles of both acetic acid and water. The number of moles of acetic acid is 0.0629 mol, as calculated in part (a). We know that 100.0 g of vinegar contains 3.78 g of acetic acid; hence the solution also contains (100.0 g − 3.78 g) = 96.2 g of water. We have

$$moles\ \mathrm{H_2O} = \frac{96.2\ \cancel{g}\ \mathrm{H_2O}}{18.02\ \cancel{g}/mol} = 5.34\ mol\ \mathrm{H_2O}$$

The mole fraction χ of acetic acid is the ratio of the number of moles of acetic acid to the total number of moles of substances present:

$$\begin{aligned}\chi_{\mathrm{CH_3CO_2H}} &= \frac{moles\ \mathrm{CH_3CO_2H}}{moles\ \mathrm{CH_3CO_2H} + moles\ \mathrm{H_2O}} \\ &= \frac{0.0629\ mol}{0.0629\ mol + 5.34\ mol} \\ &= 0.0116 = 1.16 \times 10^{-2}\end{aligned}$$

This answer makes sense, too. There are approximately 100 times as many moles of water as moles of acetic acid, so the ratio should be approximately 0.01.

? Exercise 11.1.1: Molarity and Mole Fraction

A solution of HCl gas dissolved in water (sold commercially as “muriatic acid,” a solution used to clean masonry surfaces) has 20.22 g of HCl per 100.0 g of solution, and its density is 1.10 g/mL.

a. What is its molarity?
b. What is its mole fraction?

Answer a

6.10 M HCl

Answer b

$\chi_{HCl} = 0.111$

The concentration of a solution can also be described by its molality (m), the number of moles of solute per kilogram of solvent:

$$\text{molality (m)} = \frac{\text{moles solute}}{\text{kilogram solvent}} \tag{11.1.1}$$

Molality, therefore, has the same numerator as molarity (the number of moles of solute) but a different denominator (kilogram of solvent rather than liter of solution). For dilute aqueous solutions, the molality and molarity are nearly the same because dilute solutions are mostly solvent. Thus because the density of water under standard conditions is very close to 1.0 g/mL, the volume of 1.0 kg of H_2O under these conditions is very close to 1.0 L, and a 0.50 M solution of KBr in water, for example, has approximately the same concentration as a 0.50 m solution.

Another common way of describing concentration is as the ratio of the mass of the solute to the total mass of the solution. The result can be expressed as mass percentage, parts per million (ppm), or parts per billion (ppb):

$$\text{mass percentage} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100 \tag{11.1.2}$$

$$\text{parts per million (ppm)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \tag{11.1.3}$$

$$\text{parts per billion (ppb)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9 \tag{11.1.4}$$

In the health sciences, the concentration of a solution is often expressed as parts per thousand (ppt), indicated as a proportion. For example, adrenalin, the hormone produced in high-stress situations, is available in a 1:1000 solution, or one gram of adrenalin per

1000 g of solution.

The labels on bottles of commercial reagents often describe the contents in terms of mass percentage. Sulfuric acid, for example, is sold as a 95% aqueous solution, or 95 g of H_2SO_4 per 100 g of solution. Parts per million and parts per billion are used to describe concentrations of highly dilute solutions. These measurements correspond to milligrams and micrograms of solute per kilogram of solution, respectively. For dilute aqueous solutions, this is equal to milligrams and micrograms of solute per liter of solution (assuming a density of 1.0 g/mL).

✓ Example 11.1.2: Molarity and Mass

Several years ago, millions of bottles of mineral water were contaminated with benzene at ppm levels. This incident received a great deal of attention because the lethal concentration of benzene in rats is 3.8 ppm. A 250 mL sample of mineral water has 12.7 ppm of benzene. Because the contaminated mineral water is a very dilute aqueous solution, we can assume that its density is approximately 1.00 g/mL.

a. What is the molarity of the solution?
b. What is the mass of benzene in the sample?

Given: volume of sample, solute concentration, and density of solution

Asked for: molarity of solute and mass of solute in 250 mL

Strategy:

A. Use the concentration of the solute in parts per million to calculate the molarity.
B. Use the concentration of the solute in parts per million to calculate the mass of the solute in the specified volume of solution.

Solution:

a. A To calculate the molarity of benzene, we need to determine the number of moles of benzene in 1 L of solution. We know that the solution contains 12.7 ppm of benzene. Because 12.7 ppm is equivalent to 12.7 mg/1000 g of solution and the density of the solution is 1.00 g/mL, the solution contains 12.7 mg of benzene per liter (1000 mL). The molarity is therefore

$$\begin{aligned} \text{molarity} &= \frac{\text{moles}}{\text{liter solution}} \\ &= \frac{(12.7\ \cancel{mg})\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{1\ mol}{78.114\ \cancel{g}}\right)}{1.00\ L} \\ &= 1.63\times10^{-4} M \end{aligned}$$

b. B We are given that there are 12.7 mg of benzene per 1000 g of solution, which is equal to 12.7 mg/L of solution. Hence the mass of benzene in 250 mL (250 g) of solution is

$$\begin{aligned} \text{mass of benzene} &= \frac{(12.7\ mg\ \text{benzene})(250\ \cancel{mL})}{1000\ \cancel{mL}} \\ &= 3.18\ mg \\ &= 3.18\times10^{-3}\ g\ \text{benzene} \end{aligned}$$

? Exercise 11.1.2: Molarity of Lead Solution

The maximum allowable concentration of lead in drinking water is 9.0 ppb.

a. What is the molarity of Pb^{2+} in a 9.0 ppb aqueous solution?
b. Use your calculated concentration to determine how many grams of Pb^{2+} are in an 8 oz glass of water.

Answer a

4.3×10^{-8} M

Answer b

2×10^{-6} g

How do chemists decide which units of concentration to use for a particular application? Although molarity is commonly used to express concentrations for reactions in solution or for titrations, it does have one drawback—molarity is the number of moles of solute divided by the volume of the solution, and the volume of a solution depends on its density, which is a function of temperature. Because volumetric glassware is calibrated at a particular temperature, typically 20°C, the molarity may differ from the original value by several percent if a solution is prepared or used at a significantly different temperature, such as 40°C or 0°C. For many applications this may not be a problem, but for precise work these errors can become important. In contrast, mole fraction, molality, and mass percentage depend on only the masses of the solute and solvent, which are independent of temperature.

Mole fraction is not very useful for experiments that involve quantitative reactions, but it is convenient for calculating the partial pressure of gases in mixtures, as discussed previously. Mole fractions are also useful for calculating the vapor pressures of certain types of solutions. Molality is particularly useful for determining how properties such as the freezing or boiling point of a solution vary with solute concentration. Because mass percentage and parts per million or billion are simply different ways of expressing the ratio of the mass of a solute to the mass of the solution, they enable us to express the concentration of a substance even when the molecular mass of the substance is unknown. Units of ppb or ppm are also used to express very low concentrations, such as those of residual impurities in foods or of pollutants in environmental studies.

Table 11.1.1 summarizes the different units of concentration and typical applications for each. When the molar mass of the solute and the density of the solution are known, it becomes relatively easy with practice to convert among the units of concentration we have discussed, as illustrated in Example 11.1.3.

Table 11.1.1: Different Units for Expressing the Concentrations of Solutions*

Unit	Definition	Application
molarity (M)	moles of solute/liter of solution (mol/L)	Used for quantitative reactions in solution and titrations; mass and molecular mass of solute and volume of solution are known.
mole fraction (χ)	moles of solute/total moles present (mol/mol)	Used for partial pressures of gases and vapor pressures of some solutions; mass and molecular mass of each component are known.
molality (m)	moles of solute/kg of solvent (mol/kg)	Used in determining how colligative properties vary with solute concentration; masses and molecular mass of solute are known.
mass percentage (%)	[mass of solute (g)/mass of solution (g)] × 100	Useful when masses are known but molecular masses are unknown.
parts per thousand (ppt)	[mass of solute/mass of solution] × 10^3 (g solute/kg solution)	Used in the health sciences, ratio solutions are typically expressed as a proportion, such as 1:1000.
parts per million (ppm)	[mass of solute/mass of solution] × 10^6 (mg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.
parts per billion (ppb)	[mass of solute/mass of solution] × 10^9 (µg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.

*The molarity of a solution is temperature dependent, but the other units shown in this table are independent of temperature.

✓ Example 11.1.3: Vodka

Vodka is essentially a solution of ethanol in water. Typical vodka is sold as "80 proof," which means that it contains 40.0% ethanol by volume. The density of pure ethanol is 0.789 g/mL at 20°C. If we assume that the volume of the solution is the sum of the volumes of the components (which is not strictly correct), calculate the following for the ethanol in 80-proof vodka.

a. the mass percentage
b. the mole fraction
c. the molarity
d. the molality

Given: volume percent and density

Asked for: mass percentage, mole fraction, molarity, and molality

Strategy:

A. Use the density of the solute to calculate the mass of the solute in 100.0 mL of solution. Calculate the mass of water in 100.0 mL of solution.
B. Determine the mass percentage of solute by dividing the mass of ethanol by the mass of the solution and multiplying by 100.
C. Convert grams of solute and solvent to moles of solute and solvent. Calculate the mole fraction of solute by dividing the moles of solute by the total number of moles of substances present in solution.
D. Calculate the molarity of the solution: moles of solute per liter of solution. Determine the molality of the solution by dividing the number of moles of solute by the kilograms of solvent.

Solution:

The key to this problem is to use the density of pure ethanol to determine the mass of ethanol (CH_3CH_2OH), abbreviated as EtOH, in a given volume of solution. We can then calculate the number of moles of ethanol and the concentration of ethanol in any of the required units. A Because we are given a percentage by volume, we assume that we have 100.0 mL of solution. The volume of ethanol will thus be 40.0% of 100.0 mL, or 40.0 mL of ethanol, and the volume of water will be 60.0% of 100.0 mL, or 60.0 mL of water. The mass of ethanol is obtained from its density:

$$mass\ of\ EtOH = (40.0\ \ m\cancel{L}) \left(\frac{0.789\ g}{m\cancel{L}} \right) = 31.6\ g\ EtOH$$

If we assume the density of water is 1.00 g/mL, the mass of water is 60.0 g. We now have all the information we need to calculate the concentration of ethanol in the solution.

B The mass percentage of ethanol is the ratio of the mass of ethanol to the total mass of the solution, expressed as a percentage:

$$\begin{aligned} \%EtOH &= \left(\frac{mass\ of\ EtOH}{mass\ of\ solution} \right) (100) \\ &= \left(\frac{31.6\ \ \cancel{g}\ EtOH}{31.6\ \ \cancel{g}\ EtOH + 60.0\ \ \cancel{g}\ H_2O} \right) (100) \\ &= 34.5\% \end{aligned}$$

C The mole fraction of ethanol is the ratio of the number of moles of ethanol to the total number of moles of substances in the solution. Because 40.0 mL of ethanol has a mass of 31.6 g, we can use the molar mass of ethanol (46.07 g/mol) to determine the number of moles of ethanol in 40.0 mL:

$$\begin{aligned} moles\ \mathrm{CH_3CH_2OH} &= (31.6\ \ g\ \cancel{\mathrm{CH_3CH_2OH}}) \left(\frac{1\ mol}{46.07\ \ g\ \cancel{\mathrm{CH_3CH_2OH}}} \right) \\ &= 0.686\ mol\ \mathrm{CH_3CH_2OH} \end{aligned}$$

Similarly, the number of moles of water is

$$moles\ \mathrm{H_2O} = (60.0\ \ g\ \cancel{\mathrm{H_2O}}) \left(\frac{1\ mol\ \mathrm{H_2O}}{18.02\ \ g\ \cancel{\mathrm{H_2O}}}\right) = 3.33\ mol\ \mathrm{H_2O}$$

The mole fraction of ethanol is thus

$$\chi_{\mathrm{CH_3CH_2OH}} = \frac{0.686\ \ \cancel{mol}}{0.686\ \ \cancel{mol} + 3.33\ \ \cancel{mol}} = 0.171$$

D The molarity of the solution is the number of moles of ethanol per liter of solution. We already know the number of moles of ethanol per 100.0 mL of solution, so the molarity is

$$M_{\mathrm{CH_3CH_2OH}} = \left(\frac{0.686\ mol}{100\ \ \cancel{mL}}\right)\left(\frac{1000\ \ \cancel{mL}}{L}\right) = 6.86\ M$$

The molality of the solution is the number of moles of ethanol per kilogram of solvent. Because we know the number of moles of ethanol in 60.0 g of water, the calculation is again straightforward:

$$m_{\mathrm{CH_3CH_2OH}} = \left(\frac{0.686\ mol\ EtOH}{60.0\ \ \cancel{g}\ H_2O}\right)\left(\frac{1000\ \ \cancel{g}}{kg}\right) = \frac{11.4\ mol\ EtOH}{kg\ H_2O} = 11.4\ m$$

Exercise 11.1.3: Toluene/Benzene Solution

A solution is prepared by mixing 100.0 mL of toluene with 300.0 mL of benzene. The densities of toluene and benzene are 0.867 g/mL and 0.874 g/mL, respectively. Assume that the volume of the solution is the sum of the volumes of the components. Calculate the following for toluene.

a. mass percentage
b. mole fraction
c. molarity
d. molality

Answer a

mass percentage toluene = 24.8%

Answer b

$\chi_{toluene} = 0.219$

Answer c

2.35 M toluene

Answer d

3.59 m toluene

A Video Discussing Different Measures of Concentration. Video Link: Measures of Concentration, YouTube (opens in new window) [youtu.be]

A Video Discussing how to Convert Measures of Concentration. Video Link: Converting Units of Concentration, YouTube(opens in new window) [youtu.be]

Summary

Different units are used to express the concentrations of a solution depending on the application. The concentration of a solution is the quantity of solute in a given quantity of solution. It can be expressed in several ways: molarity (moles of solute per liter of solution); mole fraction, the ratio of the number of moles of solute to the total number of moles of substances present; mass percentage, the ratio of the mass of the solute to the mass of the solution times 100; parts per thousand (ppt), grams of solute per kilogram of solution; parts per million (ppm), milligrams of solute per kilogram of solution; parts per billion (ppb), micrograms of solute per kilogram of solution; and molality (m), the number of moles of solute per kilogram of solvent.

11.2: Nature of Dissolved Species

Learning Objectives

- To understand how enthalpy and entropy changes affect solution formation.
- To use the magnitude of the changes in both enthalpy and entropy to predict whether a given solute–solvent combination will spontaneously form a solution.

In all solutions, whether gaseous, liquid, or solid, the substance present in the greatest amount is the solvent, and the substance or substances present in lesser amounts are the solute(s). The solute does not have to be in the same physical state as the solvent, but the physical state of the solvent usually determines the state of the solution. As long as the solute and solvent combine to give a homogeneous solution, the solute is said to be soluble in the solvent. Table $11.2.1$ lists some common examples of gaseous, liquid, and solid solutions and identifies the physical states of the solute and solvent in each.

Table 11.2.1: Types of Solutions

Solution	Solute	Solvent	Examples
gas	gas	gas	air, natural gas
liquid	gas	liquid	seltzer water (CO_2 gas in water)
liquid	liquid	liquid	alcoholic beverage (ethanol in water), gasoline
liquid	solid	liquid	tea, salt water
solid	gas	solid	H_2 in Pd (used for H_2 storage)
solid	solid	liquid	mercury in silver or gold (amalgam often used in dentistry)
solid	solid	solid	alloys and other "solid solutions"

Forming a Solution

The formation of a solution from a solute and a solvent is a physical process, not a chemical one. That is, both solute and solvent can be recovered in chemically unchanged forms using appropriate separation methods. For example, solid zinc nitrate dissolves in water to form an aqueous solution of zinc nitrate:

$$\mathrm{Zn(NO_3)_2(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2\,NO_3^-(aq)} \tag{11.2.1}$$

Because $Zn(NO_3)_2$ can be recovered easily by evaporating the water, this is a physical process. In contrast, metallic zinc appears to dissolve in aqueous hydrochloric acid. In fact, the two substances undergo a chemical reaction to form an aqueous solution of zinc chloride with evolution of hydrogen gas:

$$\mathrm{Zn(s) + 2\,H^+(aq) + 2\,Cl^-(aq) \rightarrow Zn^{2+}(aq) + 2\,Cl^-(aq) + H_2(g)} \tag{11.2.2}$$

When the solution evaporates, we do not recover metallic zinc, so we cannot say that metallic zinc is soluble in aqueous hydrochloric acid because it is chemically transformed when it dissolves. The dissolution of a solute in a solvent to form a solution does not involve a chemical transformation (that it is a physical change).

> *Dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.*

Substances that form a single homogeneous phase in all proportions are said to be completely *miscible* in one another. Ethanol and water are miscible, just as mixtures of gases are miscible. If two substances are essentially insoluble in each other, such as oil and water, they are *immiscible*. Examples of gaseous solutions that we have already discussed include Earth's atmosphere.

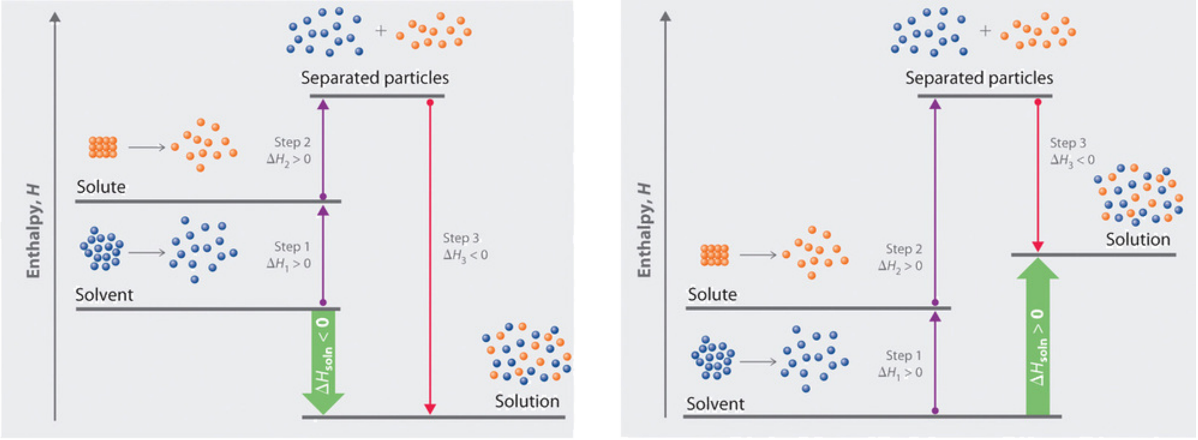
The Role of Enthalpy in Solution Formation

Energy is required to overcome the intermolecular interactions in a solute, which can be supplied only by the new interactions that occur in the solution, when each solute particle is surrounded by particles of the solvent in a process called solvation (or hydration when the solvent is water). Thus all of the solute–solute interactions and many of the solvent–solvent interactions must be disrupted for a solution to form. In this section, we describe the role of enthalpy in this process.

Because enthalpy is a state function, we can use a thermochemical cycle to analyze the energetics of solution formation. The process occurs in three discrete steps, indicated by ΔH_1, ΔH_2, and ΔH_3 in Figure 11.2.2. The overall enthalpy change in the formation of the solution (ΔH_{soln}) is the sum of the enthalpy changes in the three steps:

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3 \tag{11.2.3}$$

When a solvent is added to a solution, steps 1 and 2 are both endothermic because energy is required to overcome the intermolecular interactions in the solvent (ΔH_1) and the solute (ΔH_2). Because ΔH is positive for both steps 1 and 2, the solute–solvent interactions (ΔH_3) must be stronger than the solute–solute and solvent–solvent interactions they replace in order for the dissolution process to be exothermic ($\Delta H_{soln} < 0$). When the solute is an ionic solid, ΔH_2 corresponds to the lattice energy that must be overcome to form a solution. The higher the charge of the ions in an ionic solid, the higher the lattice energy. Consequently, solids that have very high lattice energies, such as MgO (−3791 kJ/mol), are generally insoluble in all solvents.



(a) Exothermic solution formation **(b) Endothermic solution formation**

Figure 11.2.2: Enthalpy Changes That Accompany the Formation of a Solution. Solvation can be an exothermic or endothermic process depending on the nature of the solute and solvent. In both cases, step 1, separation of the solvent particles, is energetically uphill ($\Delta H_1 > 0$), as is step 2, separation of the solute particles ($\Delta H_2 > 0$). In contrast, energy is released in step 3 ($\Delta H_3 < 0$) because of interactions between the solute and solvent. (a) When ΔH_3 is larger in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is exothermic ($\Delta H_{soln} < 0$), as shown in the thermochemical cycle. (b) When ΔH_3 is smaller in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is endothermic ($\Delta H_{soln} > 0$).

A positive value for ΔH_{soln} does not mean that a solution will not form. Whether a given process, including formation of a solution, occurs spontaneously depends on whether the total energy of the system is lowered as a result. Enthalpy is only one of the contributing factors. A high ΔH_{soln} is usually an indication that the substance is not very soluble. Instant cold packs used to treat athletic injuries, for example, take advantage of the large positive ΔH_{soln} of ammonium nitrate during dissolution (+25.7 kJ/mol), which produces temperatures less than 0°C (Figure 11.2.3).

Figure 11.2.3: Commercial Cold Packs for Treating Injuries. These packs contain solid NH_4NO_3 and water in separate compartments. When the seal between the compartments is broken, the NH_4NO_3 dissolves in the water. Because ΔH_{soln} for NH_4NO_3 is much greater than zero, heat is absorbed by the cold pack during the dissolution process, producing local temperatures less than 0°C.

Entropy and Solution Formation

The enthalpy change that accompanies a process is important because processes that release substantial amounts of energy tend to occur spontaneously. A second property of any system, its entropy, is also important in helping us determine whether a given process occurs spontaneously. We will discuss entropy in more detail elsewhere, but for now we can state that entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. A perfect crystal at 0 K, whose atoms are regularly arranged in a perfect lattice and are motionless, has an entropy of zero. In contrast, gases have large positive entropies because their molecules are highly disordered and in constant motion at high speeds.

The formation of a solution disperses molecules, atoms, or ions of one kind throughout a second substance, which generally increases the disorder and results in an increase in the entropy of the system. Thus entropic factors almost always favor formation of a solution. In contrast, a change in enthalpy may or may not favor solution formation. The London dispersion forces that hold cyclohexane and n-hexane together in pure liquids, for example, are similar in nature and strength. Consequently, ΔH_{soln} should be approximately zero, as is observed experimentally. Mixing equal amounts of the two liquids, however, produces a solution in which the n-hexane and cyclohexane molecules are uniformly distributed over approximately twice the initial volume. In this case, the driving force for solution formation is not a negative ΔH_{soln} but rather the increase in entropy due to the increased disorder in the mixture. All spontaneous processes with $\Delta H \geq 0$ are characterized by an *increase* in entropy. In other cases, such as mixing oil with water, salt with gasoline, or sugar with hexane, the enthalpy of solution is large and positive, and the increase in entropy resulting from solution formation is not enough to overcome it. Thus in these cases a solution does not form.

> *All spontaneous processes with $\Delta H \geq 0$ are characterized by an increase in entropy.*

Table $11.2.2$ summarizes how enthalpic factors affect solution formation for four general cases. The column on the far right uses the relative magnitudes of the enthalpic contributions to predict whether a solution will form from each of the four. Keep in mind that in each case entropy favors solution formation. In two of the cases the enthalpy of solution is expected to be relatively small and can be either positive or negative. Thus the entropic contribution dominates, and we expect a solution to form readily. In the other two cases the enthalpy of solution is expected to be large and positive. The entropic contribution, though favorable, is usually too small to overcome the unfavorable enthalpy term. Hence we expect that a solution will not form readily.

Table 11.2.2: Relative Changes in Enthalpies for Different Solute–Solvent Combinations*

ΔH_1 (separation of solvent molecules)	ΔH_2 (separation of solute particles)	ΔH_3 (solute–solvent interactions)	ΔH_{soln} (ΔH_1 + ΔH_2 +ΔH_3)	Result of Mixing Solute and Solvent†
large; positive	large; positive	large; negative	small; positive or negative	solution will usually form
small; positive	large; positive	small; negative	large; positive	solution will not form
large; positive	small; positive	small; negative	large; positive	solution will not form

ΔH_1 (separation of solvent molecules)	ΔH_2 (separation of solute particles)	ΔH_3 (solute–solvent interactions)	ΔH_{soln} (ΔH_1 + ΔH_2 +ΔH_3)	Result of Mixing Solute and Solvent†
small; positive	small; positive	small; negative	small; positive or negative	solution will usually form

*ΔH_1, ΔH_2, and ΔH_3 refer to the processes indicated in the thermochemical cycle shown in Figure 11.2.2.
†In all four cases, entropy increases.

In contrast to liquid solutions, the intermolecular interactions in gases are weak (they are considered to be nonexistent in ideal gases). Hence mixing gases is usually a thermally neutral process ($\Delta H_{soln} \approx 0$), and the entropic factor due to the increase in disorder is dominant (Figure 11.2.4). Consequently, all gases dissolve readily in one another in all proportions to form solutions.

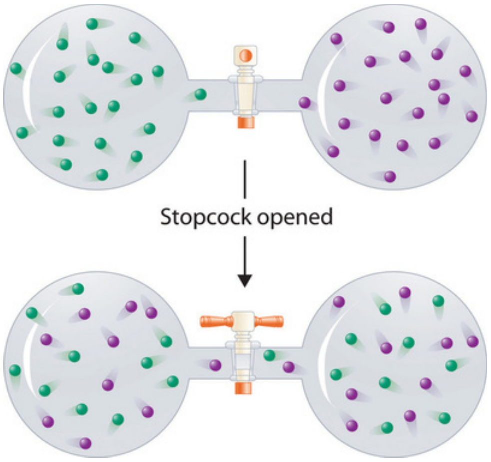
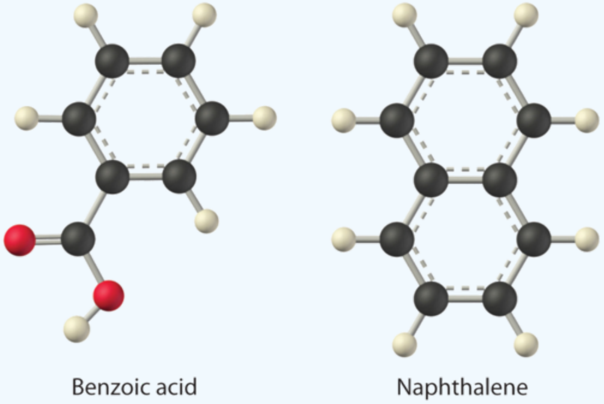


Figure 11.2.4: Formation of a Solution of Two Gases. (top) Pure samples of two different gases are in separate bulbs. (bottom) When the connecting stopcock is opened, diffusion causes the two gases to mix together and form a solution. Even though ΔH_{soln} is zero for the process, the increased entropy of the solution (the increased disorder) versus that of the separate gases favors solution formation.

Example 11.2.1

Considering $LiCl$, benzoic acid ($C_6H_5CO_2H$), and naphthalene, which will be most soluble and which will be least soluble in water?



Given: three compounds

Asked for: relative solubilities in water

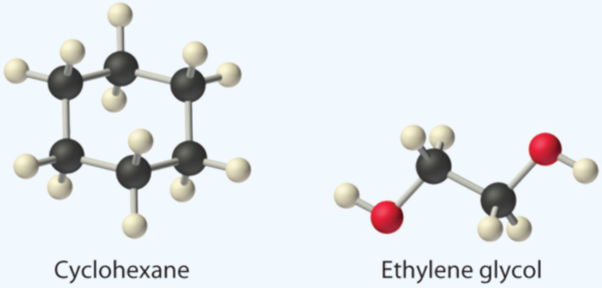
Strategy: Assess the relative magnitude of the enthalpy change for each step in the process shown in Figure 11.2.2. Then use Table 11.2.2 to predict the solubility of each compound in water and arrange them in order of decreasing solubility.

Solution:

The first substance, LiCl, is an ionic compound, so a great deal of energy is required to separate its anions and cations and overcome the lattice energy (ΔH_2 is far greater than zero in Equation 11.2.1). Because water is a polar substance, the interactions between both Li^+ and Cl^- ions and water should be favorable and strong. Thus we expect ΔH_3 to be far less than zero, making LiCl soluble in water. In contrast, naphthalene is a nonpolar compound, with only London dispersion forces holding the molecules together in the solid state. We therefore expect ΔH_2 to be small and positive. We also expect the interaction between polar water molecules and nonpolar naphthalene molecules to be weak $\Delta H_3 \approx 0$. Hence we do not expect naphthalene to be very soluble in water, if at all. Benzoic acid has a polar carboxylic acid group and a nonpolar aromatic ring. We therefore expect that the energy required to separate solute molecules (ΔH_2) will be greater than for naphthalene and less than for LiCl. The strength of the interaction of benzoic acid with water should also be intermediate between those of LiCl and naphthalene. Hence benzoic acid is expected to be more soluble in water than naphthalene but less soluble than LiCl. We thus predict LiCl to be the most soluble in water and naphthalene to be the least soluble.

? Exercise 11.2.1

Considering ammonium chloride, cyclohexane, and ethylene glycol ($HOCH_2CH_2OH$), which will be most soluble and which will be least soluble in benzene?



Answer

The most soluble is cyclohexane; the least soluble is ammonium chloride.

Summary

Solutions are homogeneous mixtures of two or more substances whose components are uniformly distributed on a microscopic scale. The component present in the greatest amount is the solvent, and the components present in lesser amounts are the solute(s). The formation of a solution from a solute and a solvent is a physical process, not a chemical one. Substances that are miscible, such as gases, form a single phase in all proportions when mixed. Substances that form separate phases are immiscible. Solvation is the process in which solute particles are surrounded by solvent molecules. When the solvent is water, the process is called hydration. The overall enthalpy change that accompanies the formation of a solution, ΔH_{soln}, is the sum of the enthalpy change for breaking the intermolecular interactions in both the solvent and the solute and the enthalpy change for the formation of new solute–solvent interactions. Exothermic ($\Delta H_{soln} < 0$) processes favor solution formation. In addition, the change in entropy, the degree of disorder of the system, must be considered when predicting whether a solution will form. An increase in entropy (a decrease in order) favors dissolution.

11.3: Reaction Stoichiometry in Solutions: Acid-Base Titrations

Learning Objectives

- Interpret titration curves for strong and weak acid-base systems
- Compute sample pH at important stages of a titration
- Explain the function of acid-base indicators

As seen in the chapter on the stoichiometry of chemical reactions, titrations can be used to quantitatively analyze solutions for their acid or base concentrations. In this section, we will explore the changes in the concentrations of the acidic and basic species present in a solution during the process of a titration.

Titration Curves

Previously, when we studied acid-base reactions in solution, we focused only on the point at which the acid and base were stoichiometrically equivalent. No consideration was given to the pH of the solution before, during, or after the neutralization.

✓ Example 11.3.1: Calculating pH for Titration Solutions: Strong Acid/Strong Base

A titration is carried out for 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* of a strong base NaOH the titration curve is shown in Figure $11.3.1$. Calculate the pH at these volumes of added base solution:

a. 0.00 mL
b. 12.50 mL
c. 25.00 mL
d. 37.50 mL

Solution

Since HCl is a strong acid, we can assume that all of it dissociates. The initial concentration of H_3O^+ is $[H_3O^+]_0 = 0.100\ M$. When the base solution is added, it also dissociates completely, providing $OH^−$ ions. The H_3O^+ and $OH^−$ ions neutralize each other, so only those of the two that were in excess remain, and their concentration determines the pH. Thus, the solution is initially acidic (pH < 7), but eventually all the hydronium ions present from the original acid are neutralized, and the solution becomes neutral. As more base is added, the solution turns basic.

The total initial amount of the hydronium ions is:

$$\mathrm{n(H^+)_0} = [\mathrm{H_3O^+}]_0 \times 0.02500\ \mathrm{L} = 0.002500\ \mathrm{mol}$$

Once X mL of the 0.100-*M* base solution is added, the number of moles of the $OH^−$ ions introduced is:

$$\mathrm{n(OH^-)_0} = 0.100\ M \times \mathrm{X\ mL} \times \left(\frac{1\ \mathrm{L}}{1000\ \mathrm{mL}}\right)$$

The total volume becomes:

$$V = (25.00\ \mathrm{mL} + \mathrm{X\ mL})\left(\frac{1\ \mathrm{L}}{1000\ \mathrm{mL}}\right)$$

The number of moles of H_3O^+ becomes:

$$\mathrm{n(H^+)} = \mathrm{n(H^+)_0} - \mathrm{n(OH^-)_0} = 0.002500\ \mathrm{mol} - 0.100\ M \times \mathrm{X\ mL} \times \left(\frac{1\ \mathrm{L}}{1000\ \mathrm{mL}}\right)$$

The concentration of H_3O^+ is:

$$[\mathrm{H_3O^+}] = \frac{\mathrm{n(H^+)}}{\mathrm{V}} = \frac{0.002500\ \mathrm{mol} - 0.100\ M \times \mathrm{X\ mL} \times \left(\frac{1\ \mathrm{L}}{1000\ \mathrm{mL}}\right)}{(25.00\ \mathrm{mL} + \mathrm{X\ mL})\left(\frac{1\ \mathrm{L}}{1000\ \mathrm{mL}}\right)}$$

$$= \frac{0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) - 0.100 \ M \times \text{X mL}}{25.00 \text{ mL} + \text{X mL}}$$

with the definition of pH:

$$\text{pH} = -\log([\text{H}_3\text{O}^+]) \tag{11.3.1}$$

The preceding calculations work if $\text{n}(\text{H}^+)_0 - \text{n}(\text{OH}^-)_0 > 0$ and so $\text{n(H}^+) > 0$. When $\text{n}(\text{H}^+)_0 = \text{n}(\text{OH}^-)_0$, the H_3O^+ ions from the acid and the OH^- ions from the base mutually neutralize. At this point, the only hydronium ions left are those from the autoionization of water, and there are no OH^- particles to neutralize them. Therefore, in this case:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-], \ [\text{H}_3\text{O}^+] = K_\text{w} = 1.0 \times 10^{-14}; \ [\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}$$

$$\text{pH} = -\log(1.0 \times 10^{-7}) = 7.00$$

Finally, when $\text{n}(\text{OH}^-)_0 > \text{n}(\text{H}^+)_0$, there are not enough H_3O^+ ions to neutralize all the OH^- ions, and instead of $\text{n}(\text{H}^+) = \text{n}(\text{H}^+)_0 - \text{n}(\text{OH}^-)_0$, we calculate: $\text{n}(\text{OH}^-) = \text{n}(\text{OH}^-)_0 - \text{n}(\text{H}^+)_0$

In this case:

$$[\text{OH}^-] = \frac{\text{n}(\text{OH}^-)}{V} = \frac{0.100 \ M \times \text{X mL} \times \left(\frac{1 \text{ L}}{1000 \text{ mL}}\right) - 0.002500 \text{ mol}}{(25.00 \text{ mL} + \text{X mL}) \left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)}$$

$$= \frac{0.100 \ M \times \text{X mL} - 0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right)}{25.00 \text{ mL} + \text{X mL}}$$

then using the definition of pOH and its relationship to pH in room temperature aqueous solutios (Equation 11.3.1):

$$\begin{aligned} pH &= 14 - pOH \\ &= 14 + \log([OH^-]) \end{aligned}$$

Let us now consider the four specific cases presented in this problem:

(a) X = 0 mL

$$[\text{H}_3\text{O}^+] = \frac{\text{n}(\text{H}^+)}{V} = \frac{0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right)}{25.00 \text{ mL}} = 0.1 \ M$$

then using the definition of pH (Equation 11.3.1):

$$\begin{aligned} pH &= -\log(0.100) \\ &= 1.000 \end{aligned}$$

(b) X = 12.50 mL

$$[\text{H}_3\text{O}^+] = \frac{\text{n}(\text{H}^+)}{V} = \frac{0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) - 0.100 \ M \times 12.50 \text{ mL}}{25.00 \text{ mL} + 12.50 \text{ mL}} = 0.0333 \ M$$

then using the definition of pH (Equation 11.3.1):

$$\begin{aligned} pH &= -\log(0.0333) \\ &= 1.477 \end{aligned}$$

(c) X = 25.00 mL

Since the volumes and concentrations of the acid and base solutions are the same:

$$\text{n}(\text{H}^+)_0 = \text{n}(\text{OH}^-)_0$$

and

$$pH = 7.000$$

as described earlier.

(d) X = 37.50 mL

In this case:

$$\text{n}(\text{OH}^-)_0 > \text{n}(\text{H}^+)_0$$

$$[\text{OH}^-] = \frac{\text{n}(\text{OH}^-)}{V} = \frac{0.100\ M \times 35.70\ \text{mL} - 0.002500\ \text{mol} \times \left(\frac{1000\ \text{mL}}{1\ \text{L}}\right)}{25.00\ \text{mL} + 37.50\ \text{mL}} = 0.0200\ M$$

then using the definition of pH (Equation 11.3.1):

$$\begin{aligned}[pH &= 14 - pOH \\ &= 14 + \log([OH^-]) \\ &= 14 + \log(0.0200) \\ &= 12.30\end{aligned}$$

? Exercise 11.3.1

Calculate the pH for the strong acid/strong base titration between 50.0 mL of 0.100 M $HNO_3(aq)$ and 0.200 M NaOH (titrant) at the listed volumes of added base:

a. 0.00 mL,
b. 15.0 mL,
c. 25.0 mL, and
d. 40.0 mL.

Answer a

0.00: 1.000

Answer b

15.0: 1.5111

Answer c

25.0: 7e. Do not delete this text first.

Answer d

40.0: 12.523

In Example 11.3.1, we calculated pH at four points during a titration. Table 11.3.1 shows a detailed sequence of changes in the pH of a strong acid and a weak acid in a titration with NaOH.

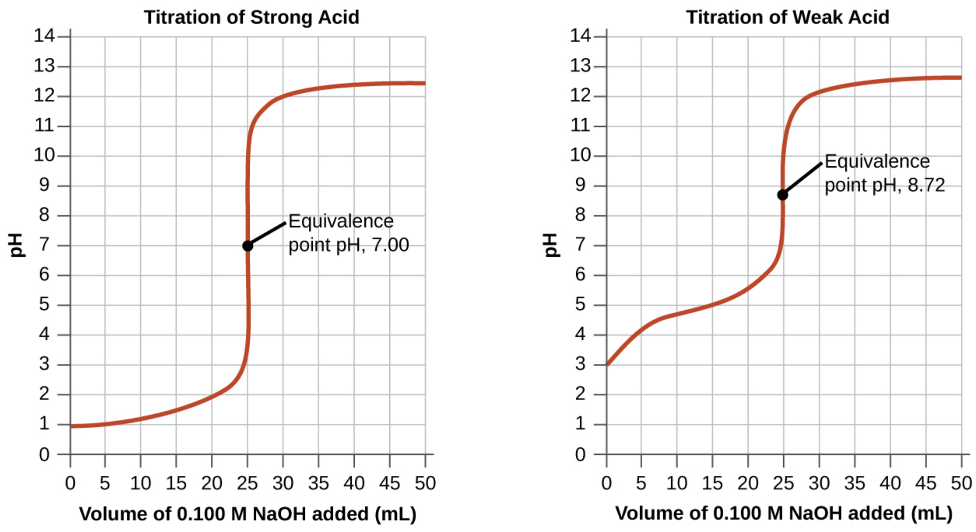
Table 11.3.1: pH Values in the Titrations of a Strong Acid with a Strong Base and of a Weak Acid with a Strong Base

Volume of 0.100 M NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 M HCl[1]	pH Values 0.100 M CH_3CO_2H[2]
0.0	0.0	1.00	2.87
5.0	0.00050	1.18	4.14
10.0	0.00100	1.37	4.57
15.0	0.00150	1.60	4.92
20.0	0.00200	1.95	5.35

Volume of 0.100 M NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 M HCl[1]	pH Values 0.100 M $CH_3CO_2H^2$
22.0	0.00220	2.20	5.61
24.0	0.00240	2.69	6.13
24.5	0.00245	3.00	6.44
24.9	0.00249	3.70	7.14
25.0	0.00250	7.00	8.72
25.1	0.00251	10.30	10.30
25.5	0.00255	11.00	11.00
26.0	0.00260	11.29	11.29
28.0	0.00280	11.75	11.75
30.0	0.00300	11.96	11.96
35.0	0.00350	12.22	12.22
40.0	0.00400	12.36	12.36
45.0	0.00450	12.46	12.46
50.0	0.00500	12.52	12.52

1. Titration of 25.00 mL of 0.100 *M* HCl (0.00250 mol of HCI) with 0.100 *M* NaOH.
2. Titration of 25.00 mL of 0.100 *M* CH_3CO_2H (0.00250 mol of CH_3CO_2H) with 0.100 *M* NaOH.

The simplest acid-base reactions are those of a strong acid with a strong base. Table $11.3.1$ shows data for the titration of a 25.0-mL sample of 0.100 *M* hydrochloric acid with 0.100 *M* sodium hydroxide. The values of the pH measured after successive additions of small amounts of NaOH are listed in the first column of this table, and are graphed in Figure $11.3.1$, in a form that is called a titration curve. The pH increases slowly at first, increases rapidly in the middle portion of the curve, and then increases slowly again. The point of inflection (located at the midpoint of the vertical part of the curve) is the equivalence point for the titration. It indicates when equivalent quantities of acid and base are present. For the titration of a strong acid with a strong base, the equivalence point occurs at a pH of 7.00 and the points on the titration curve can be calculated using solution stoichiometry (Table $11.3.1$ and Figure $11.3.1$).



(a) (b)

Figure 11.3.1: (a) The titration curve for the titration of 25.00 mL of 0.100 M HCl (strong acid) with 0.100 M NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 M CH_3CO_2H (weak acid) with 0.100 M NaOH (strong base) has an equivalence point of 8.72 pH.

Two graphs are shown. The first graph on the left is titled “Titration of Weak Acid.” The horizontal axis is labeled “Volume of 0.100 M N a O H added (m L).” Markings and vertical gridlines are provided every 5 units from 0 to 50. The vertical axis is labeled “p H” and is marked every 1 unis beginning at 0 extending to 14. A red curve is drawn on the graph which increases steadily from the point (0, 3) up to about (20, 5.5) after which the graph has a vertical section from (25, 7) up to (25, 11). The graph then levels off to a value of about 12.5 from about 40 m L up to 50 m L. The midpoint of the vertical segment of the curve is labeled “Equivalence point p H, 8.72.” The second graph on the right is titled “Titration of Strong Acid.” The horizontal axis is labeled “Volume of 0.100 M N a O H added (m L).” Markings and vertical gridlines are provided every 5 units from 0 to 50. The vertical axis is labeled “p H” and is marked every 1 units beginning at 0 extending to 14. A red curve is drawn on the graph which increases gradually from the point (0, 1) up to about (22.5, 2.2) after which the graph has a vertical section from (25, 4) up to nearly (25, 11). The graph then levels off to a value of about 12.4 from about 40 m L up to 50 m L. The midpoint of the vertical segment of the curve is labeled “Equivalence point p H, 7.00.”

The titration of a weak acid with a strong base (or of a weak base with a strong acid) is somewhat more complicated than that just discussed, but it follows the same general principles. Let us consider the titration of 25.0 mL of 0.100 *M* acetic acid (a weak acid) with 0.100 *M* sodium hydroxide and compare the titration curve with that of the strong acid. Table $11.3.1$ gives the pH values during the titration, Figure $11.3.1b$shows the titration curve.

Although the initial volume and molarity of the acids are the same, there are important differences between the two titration curves. The titration curve for the weak acid begins at a higher value (less acidic) and maintains higher pH values up to the equivalence point. This is because acetic acid is a weak acid, which is only partially ionized. The pH at the equivalence point is also higher (8.72 rather than 7.00) due to the hydrolysis of acetate, a weak base that raises the pH:

$$\mathrm{CH_3CO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2H}(l) + \mathrm{OH^-}(aq)$$

After the equivalence point, the two curves are identical because the pH is dependent on the excess of hydroxide ion in both cases.

✓ Example 11.3.2: Titration of a Weak Acid with a Strong Base

The titration curve shown in Figure $11.3.1b$is for the titration of 25.00 mL of 0.100 *M* CH_3CO_2H with 0.100 *M* NaOH. The reaction can be represented as:

$$\mathrm{CH_3CO_2H} + \mathrm{OH^-} \longrightarrow \mathrm{CH_3CO_2^-} + \mathrm{H_2O}$$

a. What is the initial pH before any amount of the NaOH solution has been added? $K_a = 1.8 \times 10^{-5}$ for CH_3CO_2H.
b. Find the pH after 25.00 mL of the NaOH solution have been added.
c. Find the pH after 12.50 mL of the NaOH solution has been added.
d. Find the pH after 37.50 mL of the NaOH solution has been added.

Solution

(a) Assuming that the dissociated amount is small compared to 0.100 *M*, we find that:

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} \approx \frac{[H_3O^+]^2}{[CH_3CO_2H]_0}$$

and

$$[H_3O^+] = \sqrt{K_a \times [CH_3CO_2H]} = \sqrt{1.8 \times 10^{-5} \times 0.100} = 1.3 \times 10^{-3}$$

$$pH = -\log(1.3 \times 10^{-3}) = 2.87$$

(b) After 25.00 mL of NaOH are added, the number of moles of NaOH and CH_3CO_2H are equal because the amounts of the solutions and their concentrations are the same. All of the CH_3CO_2H has been converted to $CH_3CO_2^-$. The concentration of the $CH_3CO_2^-$ ion is:

$$\frac{0.00250 \text{ mol}}{0.0500 \text{ L}} = 0.0500 \text{ M} CH_3CO_2^-$$

The equilibrium that must be focused on now is the basicity equilibrium for $CH_3CO_2^-$:

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

so we must determine K_b for the base by using the ion product constant for water:

$$K_b = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2^-]}$$

$$K_a = \frac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]}, \text{ so } \frac{[CH_3CO_2H]}{[CH_3CO_2^-]} = \frac{[H^+]}{K_a}.$$

Since $K_w = [H^+][OH^-]$:

$$K_b = \frac{[H^+][OH^-]}{K_a} \tag{11.3.2}$$

$$= \frac{K_w}{K_a} \tag{11.3.3}$$

$$= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \tag{11.3.4}$$

$$= 5.6 \times 10^{-10} \tag{11.3.5}$$

Let us denote the concentration of each of the products of this reaction, CH_3CO_2H and OH^-, as *x*. Using the assumption that *x* is small compared to 0.0500 *M*, $K_b = \frac{x^2}{0.0500\ M}$, and then:

$$x = [OH^-] = 5.3 \times 10^{-6}$$

$$pOH = -\log(5.3 \times 10^{-6}) = 5.28$$

$$pH = 14.00 - 5.28 = 8.72$$

Note that the pH at the equivalence point of this titration is significantly greater than 7.

(c) In (a), 25.00 mL of the NaOH solution was added, and so practically all the CH_3CO_2H was converted into $CH_3CO_2^-$. In this case, only 12.50 mL of the base solution has been introduced, and so only half of all the CH_3CO_2H is converted into $CH_3CO_2^-$. The total initial number of moles of CH_3CO_2H is 0.02500L × 0.100 <u>*M*</u> = 0.00250 mol, and so after adding the NaOH, the numbers of moles of CH_3CO_2H and $CH_3CO_2^-$ are both approximately equal to $\frac{0.00250 \text{ mol}}{2} = 0.00125 \text{ mol}$, and their concentrations are the same.

Since the amount of the added base is smaller than the original amount of the acid, the equivalence point has not been reached, the solution remains a buffer, and we can use the Henderson-Hasselbalch equation:

$$\mathrm{pH}=\mathrm{p}K_\mathrm{a}+\log\frac{[\mathrm{Base}]}{[\mathrm{Acid}]}=-\log(K_\mathrm{a})+\log\frac{[\mathrm{CH_3CO_2^-}]}{[\mathrm{CH_3CO_2H}]}=-\log(1.8\times10^{-5})+\log(1)$$

(as the concentrations of $\mathrm{CH_3CO_2^-}$ and CH_3CO_2H are the same)

Thus:

$$\mathrm{pH}=-\log(1.8\times10^{-5})=4.74$$

(the pH = the pK_a at the halfway point in a titration of a weak acid)

(d) After 37.50 mL of NaOH is added, the amount of NaOH is 0.03750 L × 0.100 *M* = 0.003750 mol NaOH. Since this is past the equivalence point, the excess hydroxide ions will make the solution basic, and we can again use stoichiometric calculations to determine the pH:

$$[\mathrm{OH^-}]=\frac{(0.003750\ \mathrm{mol}-0.00250\ \mathrm{mol})}{0.06250\ \mathrm{L}}=2.00\times10^{-2}\ M$$

So:

$$\mathrm{pOH}=-\log(2.00\times10^{-2})=1.70,\ \text{and}\ \mathrm{pH}=14.00-1.70=12.30$$

Note that this result is the same as for the strong acid-strong base titration example provided, since the amount of the strong base added moves the solution past the equivalence point.

? Exercise 11.3.2

Calculate the pH for the weak acid/strong base titration between 50.0 mL of 0.100 *M* HCOOH(*aq*) (formic acid) and 0.200 *M* NaOH (titrant) at the listed volumes of added base:

a. 0.00 mL,
b. 15.0 mL,
c. 25.0 mL, and
d. 30.0 mL.

Answer a

0.00 mL: 2.37

Answer b

15.0 mL: 3.92

Answer c

25.00 mL: 8.29

Answer d

30.0 mL: 12.097

Acid-Base Indicators

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colorless substance in any aqueous solution with a hydronium ion concentration greater than 5.0 × 10^{-9} *M* (pH < 8.3). In more basic solutions where the hydronium ion concentration is less than 5.0 × 10^{-9} *M* (pH > 8.3), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called acid-base indicators. Acid-base indicators are either weak organic acids or weak organic bases.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use HIn as a simple representation for the complex methyl orange molecule:

$$\underbrace{\mathrm{HIn(aq)}}_{\text{red}}+\mathrm{H_2O(l)}\rightleftharpoons\mathrm{H_3O^+(aq)}+\underbrace{\mathrm{In^-(aq)}}_{\text{yellow}}$$

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{In^-}]}{[\mathrm{HIn}]} = 4.0 \times 10^{-4}$$

The anion of methyl orange, $\mathrm{In^-}$, is yellow, and the nonionized form, HIn, is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Chatelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

An indicator's color is the visible result of the ratio of the concentrations of the two species $\mathrm{In^-}$ and HIn. If most of the indicator (typically about 60−90% or more) is present as $\mathrm{In^-}$, then we see the color of the $\mathrm{In^-}$ ion, which would be yellow for methyl orange. If most is present as HIn, then we see the color of the HIn molecule: red for methyl orange. For methyl orange, we can rearrange the equation for K_a and write:

$$\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]} = \frac{[\text{substance with yellow color}]}{[\text{substance with red color}]} = \frac{K_a}{[\mathrm{H_3O^+}]} \tag{11.3.6}$$

Equation 11.3.6 shows us how the ratio of $\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]}$ varies with the concentration of hydronium ion. The above expression describing the indicator equilibrium can be rearranged:

$$\frac{[H_3O^+]}{K_a} = \frac{[HIn]}{[In^-]} \tag{11.3.7}$$

$$\log\left(\frac{[H_3O^+]}{K_a}\right) = \log\left(\frac{[HIn]}{[In^-]}\right) \tag{11.3.8}$$

$$\log([H_3O^+]) - \log(K_a) = -\log\left(\frac{[In^-]}{[HIn]}\right) \tag{11.3.9}$$

$$-pH + pK_a = -\log\left(\frac{[In^-]}{[HIn]}\right) \tag{11.3.10}$$

$$pH = pK_a + \log\left(\frac{[In^-]}{[HIn]}\right) \tag{11.3.11}$$

or in general terms

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{11.3.12}$$

Equation 11.3.12 is the same as the *Henderson-Hasselbalch equation*, which can be used to describe the equilibrium of indicators.

When $[\mathrm{H_3O^+}]$ has the same numerical value as K_a, the ratio of $[\mathrm{In^-}]$ to $[\mathrm{HIn}]$ is equal to 1, meaning that 50% of the indicator is present in the red form (HIn) and 50% is in the yellow ionic form ($\mathrm{In^-}$), and the solution appears orange in color. When the hydronium ion concentration increases to 8×10^{-4} *M* (a pH of 3.1), the solution turns red. No change in color is visible for any further increase in the hydronium ion concentration (decrease in pH). At a hydronium ion concentration of 4×10^{-5} *M* (a pH of 4.4), most of the indicator is in the yellow ionic form, and a further decrease in the hydronium ion concentration (increase in pH) does not produce a visible color change. The pH range between 3.1 (red) and 4.4 (yellow) is the color-change interval of methyl orange; the pronounced color change takes place between these pH values.

There are many different acid-base indicators that cover a wide range of pH values and can be used to determine the approximate pH of an unknown solution by a process of elimination. Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pHs. Figure 11.3.2 presents several indicators, their colors, and their color-change intervals.

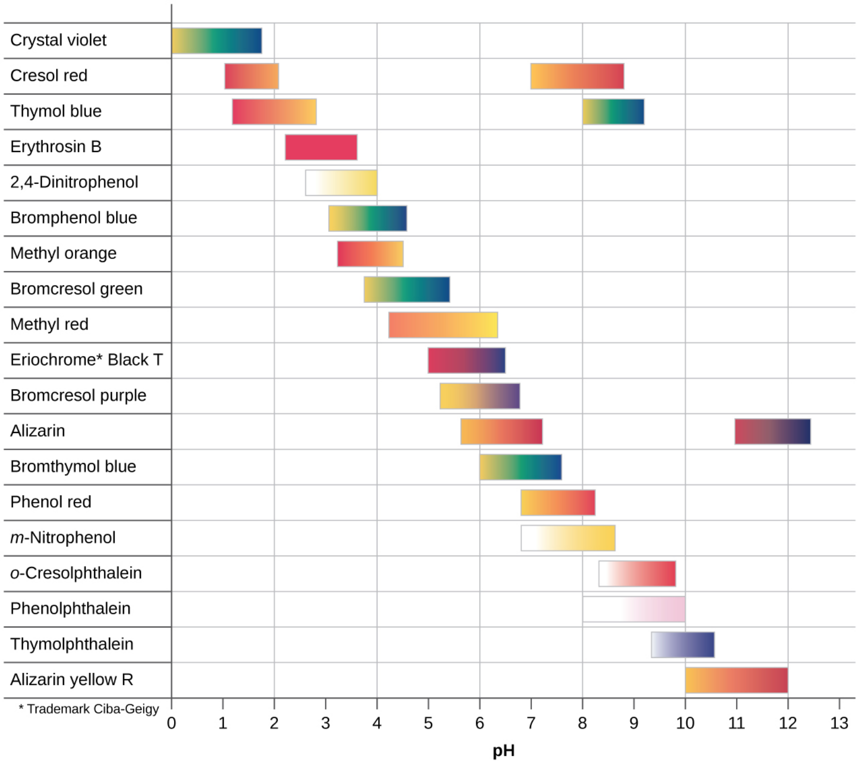


Figure 11.3.2: This chart illustrates the ranges of color change for several acid-base indicators.

Titration curves help us pick an indicator that will provide a sharp color change at the equivalence point. The best selection would be an indicator that has a color change interval that brackets the pH at the equivalence point of the titration.

The color change intervals of three indicators are shown in Figure 11.3.3. The equivalence points of both the titration of the strong acid and of the weak acid are located in the color-change interval of phenolphthalein. We can use it for titrations of either strong acid with strong base or weak acid with strong base.

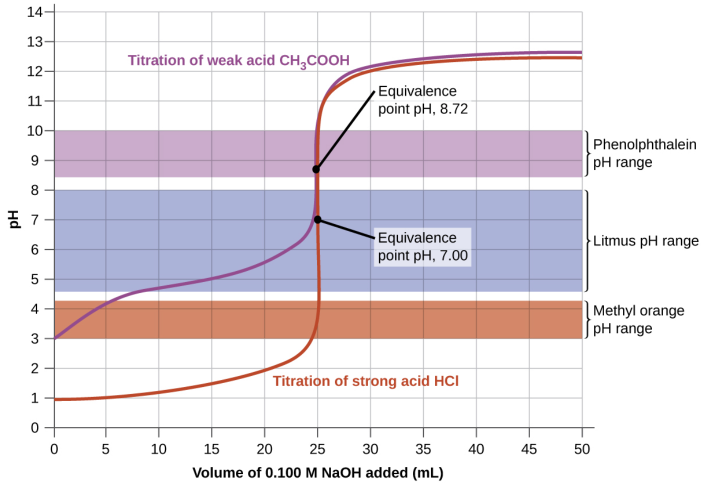


Figure $11.3.3$: The graph shows a titration curve for the titration of 25.00 mL of 0.100 M CH_3CO_2H (weak acid) with 0.100 M NaOH (strong base) and the titration curve for the titration of HCl (strong acid) with NaOH (strong base). The pH ranges for the color change of phenolphthalein, litmus, and methyl orange are indicated by the shaded areas.

A graph is shown which is titled “Titration of Weak Acid.” The horizontal axis is labeled “Volume of 0.100 M N a O H added (m L)” and begins at 0 with markings every 5 units up to 50. The vertical axis is labeled “p H” and begins at 0 and increases by single units up to 14. A red curve is drawn on the graph. The curve begins at (0, 3) and passes through the points (5, 4.1), (10, 4.7), (15, 5), (20, 5.5), and (22.5, 6), after which it rapidly increases, forming a vertical section centered at the point (25, 8.7). The rapid increase of the curve then levels off and the curve passes through the points (30, 12), (35, 12.4), (40, 12.5), (45, 12.6), and (50, 12.6). A brown rectangle extends horizontally across the graph covering the p H of 3 to 4.2 range. To the right, this rectangle is labeled “Methyl orange p H range.” A blue rectangle extends horizontally across the graph covering the p H of 4.6 to 8 range. To the right, this rectangle is labeled “Litmus p H range.” A purple rectangle extends horizontally across the graph covering the p H of 8.4 to 10 range. To the right, this rectangle is labeled “Phenolphthalein p H range.” The midpoint of the vertical segment of the curve is labeled “Equivalence point p H, 8.72.”

Litmus is a suitable indicator for the HCl titration because its color change brackets the equivalence point. However, we should not use litmus for the CH_3CO_2H titration because the pH is within the color-change interval of litmus when only about 12 mL of NaOH has been added, and it does not leave the range until 25 mL has been added. The color change would be very gradual, taking place during the addition of 13 mL of NaOH, making litmus useless as an indicator of the equivalence point.

We could use methyl orange for the HCl titration, but it would not give very accurate results: (1) It completes its color change slightly before the equivalence point is reached (but very close to it, so this is not too serious); (2) it changes color, as Figure $11.3.2$ demonstrates, during the addition of nearly 0.5 mL of NaOH, which is not so sharp a color change as that of litmus or phenolphthalein; and (3) it goes from yellow to orange to red, making detection of a precise endpoint much more challenging than the colorless to pink change of phenolphthalein. Figure $11.3.2$ shows us that methyl orange would be completely useless as an indicator for the CH_3CO_2H titration. Its color change begins after about 1 mL of NaOH has been added and ends when about 8 mL has been added. The color change is completed long before the equivalence point (which occurs when 25.0 mL of NaOH has been added) is reached and hence provides no indication of the equivalence point.

We base our choice of indicator on a calculated pH, the pH at the equivalence point. At the equivalence point, equimolar amounts of acid and base have been mixed, and the calculation becomes that of the pH of a solution of the salt resulting from the titration.

Summary

A titration curve is a graph that relates the change in pH of an acidic or basic solution to the volume of added titrant. The characteristics of the titration curve are dependent on the specific solutions being titrated. The pH of the solution at the equivalence point may be greater than, equal to, or less than 7.00. The choice of an indicator for a given titration depends on the expected pH at the equivalence point of the titration, and the range of the color change of the indicator.

Glossary

acid-base indicator

organic acid or base whose color changes depending on the pH of the solution it is in

color-change interval

range in pH over which the color change of an indicator takes place

titration curve

plot of the pH of a solution of acid or base versus the volume of base or acid added during a titration

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11.4: Reaction Stoichiometry in Solutions: Oxidation-Reduction Titrations

Analytical titrations using redox reactions were introduced shortly after the development of acid–base titrimetry. The earliest **Redox titration** took advantage of the oxidizing power of chlorine. In 1787, Claude Berthollet introduced a method for the quantitative analysis of chlorine water (a mixture of Cl_2, HCl, and HOCl) based on its ability to oxidize indigo, a dye that is colorless in its oxidized state. In 1814, Joseph Gay-Lussac developed a similar method for determining chlorine in bleaching powder. In both methods the end point is a change in color. Before the equivalence point the solution is colorless due to the oxidation of indigo. After the equivalence point, however, unreacted indigo imparts a permanent color to the solution.

The number of redox titrimetric methods increased in the mid-1800s with the introduction of MnO_4^-, $Cr_2O_7^{2-}$, and I_2 as oxidizing titrants, and of Fe^{2+} and $S_2O_3^{2-}$ as reducing titrants. Even with the availability of these new titrants, redox titrimetry was slow to develop due to the lack of suitable indicators. A titrant can serve as its own indicator if its oxidized and reduced forms differ significantly in color. For example, the intensely purple MnO_4^- ion serves as its own indicator since its reduced form, Mn^{2+}, is almost colorless. Other titrants require a separate indicator. The first such indicator, diphenylamine, was introduced in the 1920s. Other redox indicators soon followed, increasing the applicability of redox titrimetry.

Redox Titration Curves

To evaluate a redox titration we need to know the shape of its titration curve. In an acid–base titration or a complexation titration, the titration curve shows how the concentration of H_3O^+ (as pH) or M^{n+} (as pM) changes as we add titrant. For a redox titration it is convenient to monitor the titration reaction's potential instead of the concentration of one species.

You may recall from Chapter 6 that the Nernst equation relates a solution's potential to the concentrations of reactants and products participating in the redox reaction. Consider, for example, a titration in which a titrand in a reduced state, A_{red}, reacts with a titrant in an oxidized state, B_{ox}.

$$A_{\text{red}}+B_{\text{ox}} \rightleftharpoons B_{\text{red}}+A_{\text{ox}} \tag{11.4.1}$$

where A_{ox} is the titrand's oxidized form, and B_{red} is the titrant's reduced form. The reaction's potential, E_{rxn}, is the difference between the reduction potentials for each half-reaction.

$$E_{\text{rxn}}=E_{B_{\text{ox}}/B_{\text{red}}}-E_{A_{\text{ox}}/A_{\text{red}}} \tag{11.4.2}$$

After each addition of titrant the reaction between the titrand and the titrant reaches a state of equilibrium. Because the potential at equilibrium is zero, the titrand's and the titrant's reduction potentials are identical.

$$E_{B_{\text{ox}}/B_{\text{red}}}=E_{A_{\text{ox}}/A_{\text{red}}} \tag{11.4.3}$$

This is an important observation because we can use either half-reaction to monitor the titration's progress.

Before the equivalence point the titration mixture consists of appreciable quantities of the titrand's oxidized and reduced forms. The concentration of unreacted titrant, however, is very small. The potential, therefore, is easier to calculate if we use the Nernst equation for the titrand's half-reaction

$$E_{\text{rxn}}=E^{o}_{A_{\text{ox}}/A_{\text{red}}}-\frac{RT}{nF}\ln\frac{[A_{\text{red}}]}{[A_{\text{ox}}]} \tag{11.4.4}$$

Although the Nernst equation is written in terms of the half-reaction's standard state potential, a matrix-dependent **formal potential** often is used in its place. See Appendix 13 for the standard state potentials and formal potentials for selected half-reactions.

After the equivalence point it is easier to calculate the potential using the Nernst equation for the titrant's half-reaction.

$$E_{\text{rxn}}=E^{o}_{B_{\text{ox}}/B_{\text{red}}}-\frac{RT}{nF}\ln\frac{[B_{\text{red}}]}{[B_{\text{ox}}]} \tag{11.4.5}$$

Calculating the Titration Curve

Let's calculate the titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in a matrix of 1 M $HClO_4$. The reaction in this case is

$$\mathrm{Fe}^{2+}(aq)+\mathrm{Ce}^{4+}(aq) \rightleftharpoons \mathrm{Ce}^{3+}(aq)+\mathrm{Fe}^{3+}(aq) \tag{9.15}$$

In 1 M $HClO_4$, the formal potential for the reduction of Fe^{3+} to Fe^{2+} is +0.767 V, and the formal potential for the reduction of Ce^{4+} to Ce^{3+} is +1.70 V.

Because the equilibrium constant for reaction 9.15 is very large—it is approximately 6×10^{15}—we may assume that the analyte and titrant react completely.

Step 1

Calculate the volume of titrant needed to reach the equivalence point.

The first task is to calculate the volume of Ce^{4+} needed to reach the titration's equivalence point. From the reaction's stoichiometry we know that

$$\text{moles } \mathrm{Fe}^{2+}=\text{moles } \mathrm{Ce}^{4+} \tag{11.4.6}$$

$$M_{\mathrm{Fe}} \times V_{\mathrm{Fe}}=M_{\mathrm{Ce}} \times V_{\mathrm{Ce}} \tag{11.4.7}$$

Solving for the volume of Ce^{4+} gives the equivalence point volume as

$$V_{\mathrm{eq}}=V_{\mathrm{Ce}}=\frac{M_{\mathrm{Fe}} V_{\mathrm{Fe}}}{M_{\mathrm{Ce}}}=\frac{(0.100 \mathrm{~M})(50.0 \mathrm{~mL})}{(0.100 \mathrm{~M})}=50.0 \mathrm{~mL} \tag{11.4.8}$$

Step 2:

alculate the potential before the equivalence point by determining the concentrations of the titrand's oxidized and reduced forms, and using the Nernst equation for the titrand's reduction half-reaction.

Before the equivalence point, the concentration of unreacted Fe^{2+} and the concentration of Fe^{3+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Fe^{3+}/Fe^{2+} half-reaction.

$$E=E_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}}^{o}-\frac{R T}{n F} \log \frac{\left[\mathrm{Fe}^{2+}\right]}{\left[\mathrm{Fe}^{3+}\right]}=+0.767 \mathrm{V}-0.05916 \log \frac{\left[\mathrm{Fe}^{2+}\right]}{\left[\mathrm{Fe}^{3+}\right]} \tag{9.16}$$

For example, the concentrations of Fe^{2+} and Fe^{3+} after adding 10.0 mL of titrant are

$$\left[\mathrm{Fe}^{2+}\right]=\frac{\text{initial moles } \mathrm{Fe}^{2+}-\text{moles } \mathrm{Ce}^{4+} \text{ added}}{\text{total volume}}=\frac{M_{\mathrm{Fe}} V_{\mathrm{Fe}}-M_{\mathrm{Ce}} V_{\mathrm{Ce}}}{V_{\mathrm{Fe}}+V_{\mathrm{Ce}}} \tag{11.4.9}$$

$$=\frac{(0.100 \mathrm{~M})(50.0 \mathrm{~mL})-(0.100 \mathrm{~M})(10.0 \mathrm{~mL})}{50.0 \mathrm{~mL}+10.0 \mathrm{~mL}}=6.67 \times 10^{-2} \mathrm{~M} \tag{11.4.10}$$

$$\left[\mathrm{Fe}^{3+}\right]=\frac{\text{moles } \mathrm{Ce}^{4+} \text{ added}}{\text{total volume}}=\frac{M_{\mathrm{Ce}} V_{\mathrm{Ce}}}{V_{\mathrm{Fe}}+V_{\mathrm{Ce}}} \tag{11.4.11}$$

$$=\frac{(0.100 \mathrm{~M})(10.0 \mathrm{~mL})}{50.0 \mathrm{~mL}+10.0 \mathrm{~mL}}=1.67 \times 10^{-2} \mathrm{~M} \tag{11.4.12}$$

Substituting these concentrations into equation 9.16 gives a potential of

$$E=+0.767 \mathrm{~V}-0.05916 \log \frac{6.67 \times 10^{-2} \mathrm{~M}}{1.67 \times 10^{-2} \mathrm{~M}}=+0.731 \mathrm{~V} \tag{11.4.13}$$

Step 3:

Calculate the potential after the equivalence point by determining the concentrations of the titrant's oxidized and reduced forms, and using the Nernst equation for the titrant's reduction half-reaction.

After the equivalence point, the concentration of Ce^{3+} and the concentration of excess Ce^{4+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Ce^{4+}/Ce^{3+} half-reaction.

$$E=E_{\mathrm{Ce}^{4+}/\mathrm{Ce}^{3+}}^{o}-\frac{R T}{n F} \log \frac{\left[\mathrm{Ce}^{3+}\right]}{\left[\mathrm{Ce}^{4+}\right]}=+1.70 \mathrm{~V}-0.05916 \log \frac{\left[\mathrm{Ce}^{3+}\right]}{\left[\mathrm{Ce}^{4+}\right]} \tag{9.17}$$

For example, after adding 60.0 mL of titrant, the concentrations of Ce^{3+} and Ce^{4+} are

$$[\mathrm{Ce}^{3+}] = \frac{\text{initial moles Fe}^{2+}}{\text{total volume}} = \frac{M_{\mathrm{Fe}}V_{\mathrm{Fe}}}{V_{\mathrm{Fe}}+V_{\mathrm{Ce}}} \tag{11.4.14}$$

$$= \frac{(0.100\text{ M})(50.0\text{ mL})}{50.0\text{ mL}+60.0\text{ mL}} = 4.55\times10^{-3}\text{ M} \tag{11.4.15}$$

$$[\mathrm{Ce}^{4+}] = \frac{\text{moles Ce}^{4+}\text{ added} - \text{initial moles Fe}^{2+}}{\text{total volume}} = \frac{M_{\mathrm{Ce}}V_{\mathrm{Ce}} - M_{\mathrm{Fe}}V_{\mathrm{Fe}}}{V_{\mathrm{Fe}}+V_{\mathrm{Ce}}} \tag{11.4.16}$$

$$= \frac{(0.100\text{ M})(60.0\text{ mL}) - (0.100\text{ M})(50.0\text{ mL})}{50.0\text{ mL}+60.0\text{ mL}} = 9.09\times10^{-3}\text{ M} \tag{11.4.17}$$

Substituting these concentrations into Equation 9.17 gives a potential of

$$E = +1.70\text{ V} - 0.05916\log\frac{4.55\times10^{-2}\text{ M}}{9.09\times10^{-3}\text{ M}} = +1.66\text{ V} \tag{11.4.18}$$

Step 4

Calculate the potential at the equivalence point.

At the titration's equivalence point, the potential, E_{eq}, in equation 9.16 and equation 9.17 are identical. Adding the equations together to gives

$$2E_{\mathrm{eq}} = E^{o}_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}} + E^{o}_{\mathrm{Ce}^{4+}/\mathrm{Ce}^{3+}} - 0.05916\log\frac{[\mathrm{Fe}^{2+}][\mathrm{Ce}^{3+}]}{[\mathrm{Fe}^{3+}][\mathrm{Ce}^{4+}]} \tag{11.4.19}$$

Because $[Fe^{2+}] = [Ce^{4+}]$ and $[Ce^{3+}] = [Fe^{3+}]$ at the equivalence point, the log term has a value of zero and the equivalence point's potential is

$$E_{\mathrm{eq}} = \frac{E^{o}_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}} + E^{o}_{\mathrm{Ce}^{4+}/\mathrm{Ce}^{3+}}}{2} = \frac{0.767\text{ V} + 1.70\text{ V}}{2} = 1.23\text{ V} \tag{11.4.20}$$

Additional results for this titration curve are shown in Table 9.15 and Figure 9.36.

Table 9.15: *Data for the Titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}*

Volume of Ce^{4+} (mL)	*E* (V)	Volume Ce^{4+} (mL)	*E* (V)
10.0	0.731	60.0	1.66
20.0	0.757	70.0	1.68
30.0	0.777	80.0	1.69
40.0	0.803	90.0	1.69
50.0	1.23	100.0	1.70

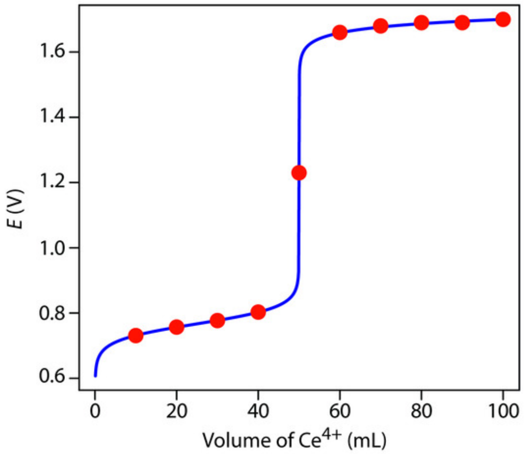


Figure 9.36 *Titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}. The red points correspond to the data in Table 9.15. The blue line shows the complete titration curve.*

Exercise 11.4.1

Calculate the titration curve for the titration of 50.0 mL of 0.0500 M Sn^{2+} with 0.100 M Tl^{3+}. Both the titrand and the titrant are 1.0 M in HCl. The titration reaction is

$$\mathrm{Sn}^{2+}(aq)+\mathrm{Tl}^{3+}(aq) \rightarrow \mathrm{Sn}^{4+}(aq)+\mathrm{Tl}^{+}(aq) \tag{11.4.21}$$

Click here to review your answer to this exercise.

Sketching a Redox Titration Curve

To evaluate the relationship between a titration's equivalence point and its end point we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching a redox titration curve. Our goal is to sketch the titration curve quickly, using as few calculations as possible. Let's use the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in a matrix of 1 M $HClO_4$.

This is the same example that we used in developing the calculations for a redox titration curve. You can review the results of that calculation in Table 9.15 and Figure 9.36.

We begin by calculating the titration's equivalence point volume, which, as we determined earlier, is 50.0 mL. Next, we draw our axes, placing the potential, *E*, on the *y*-axis and the titrant's volume on the *x*-axis. To indicate the equivalence point's volume, we draw a vertical line corresponding to 50.0 mL of Ce^{4+}. Figure 9.37a shows the result of the first step in our sketch.

Before the equivalence point, the potential is determined by a redox buffer of Fe^{2+} and Fe^{3+}. Although we can easily calculate the potential using the Nernst equation, we can avoid this calculation by making a simple assumption. You may recall from Chapter 6 that a redox buffer operates over a range of potentials that extends approximately ±(0.05916/*n*) unit on either side of $E^o_{Fe^{3+}/Fe^{2+}}$. The potential is at the buffer's lower limit

$$\mathrm{E}=E^{o}_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}}-0.05916 \tag{11.4.22}$$

when the concentration of Fe^{2+} is 10× greater than that of Fe^{3+}. The buffer reaches its upper potential

$$\mathrm{E}=E^{o}_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}}+0.05916 \tag{11.4.23}$$

when the concentration of Fe^{2+} is 10× smaller than that of Fe^{3+}. The redox buffer spans a range of volumes from approximately 10% of the equivalence point volume to approximately 90% of the equivalence point volume.

Figure 9.37b shows the second step in our sketch. First, we superimpose a ladder diagram for Fe^{2+} on the *y*-axis, using its $E^o_{Fe^{3+}/Fe^{2+}}$ value of 0.767 V and including the buffer's range of potentials. Next, we add points representing the pH at 10% of the equivalence point volume (a potential of 0.708 V at 5.0 mL) and at 90% of the equivalence point volume (a potential of 0.826 V at 45.0 mL).

> *We used a similar approach when sketching the acid–base titration curve for the titration of acetic acid with NaOH.*

The third step in sketching our titration curve is to add two points after the equivalence point. Here the potential is controlled by a redox buffer of Ce^{3+} and Ce^{4+}. The redox buffer is at its lower limit of $E = E^{o}_{Ce^{4+}/Ce^{3+}} - 0.05916$ when the titrant reaches 110% of the equivalence point volume and the potential is $E^{o}_{Ce^{4+}/Ce^{3+}}$ when the volume of Ce^{4+} is $2 \times V_{eq}$.

Figure 9.37c shows the third step in our sketch. First, we add a ladder diagram for Ce^{4+}, including its buffer range, using its $E^{o}_{Ce^{4+}/Ce^{3+}}$ value of 1.70 V. Next, we add points representing the potential at 110% of V_{eq} (a value of 1.66 V at 55.0 mL) and at 200% of V_{eq} (a value of 1.70 V at 100.0 mL).

> *We used a similar approach when sketching the complexation titration curve for the titration of Mg^{2+} with EDTA.*

Next, we draw a straight line through each pair of points, extending the line through the vertical line representing the equivalence point's volume (Figure 9.37d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure 9.37e). A comparison of our sketch to the exact titration curve (Figure 9.37f) shows that they are in close agreement.

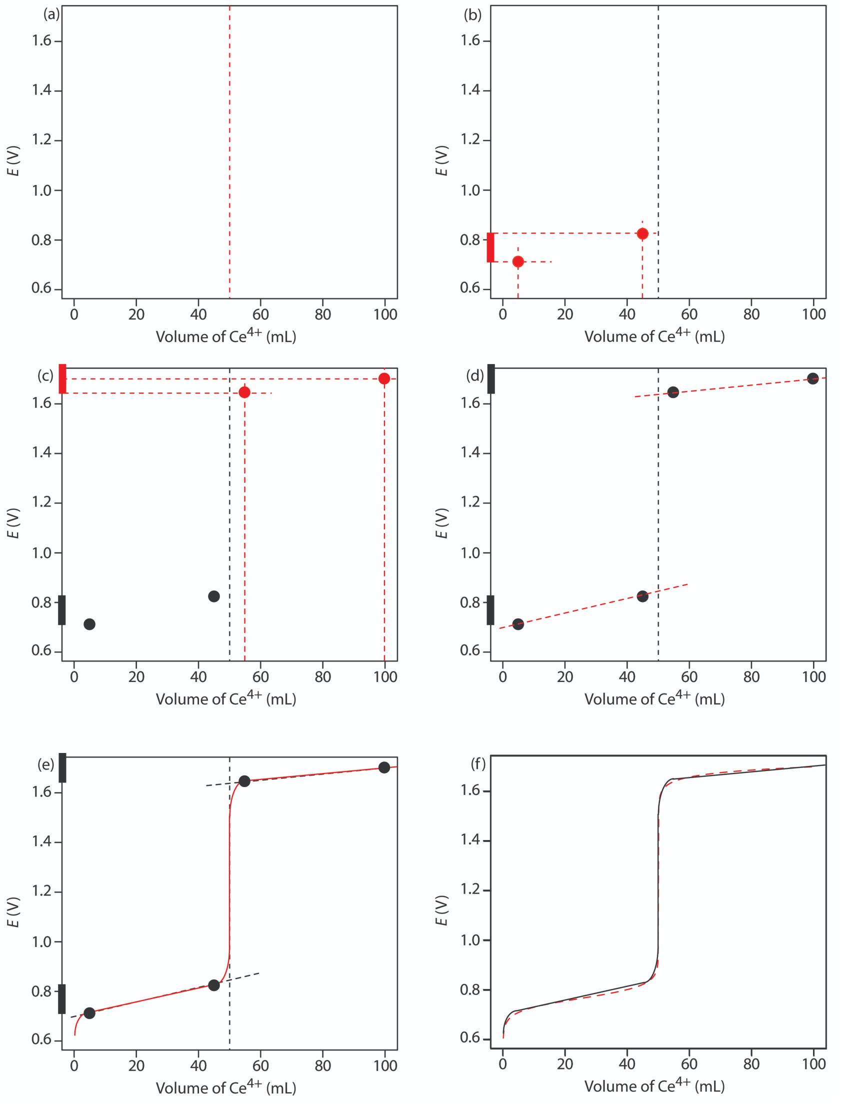


Figure 9.37: *Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in 1 M $HClO_4$: (a) locating the equivalence point volume; (b) plotting two points before the equivalence*

point; (c) plotting two points after the equivalence point; (d) preliminary approximation of titration curve using straight-lines; (e) final approximation of titration curve using a smooth curve; (f) comparison of approximate titration curve (solid black line) and exact titration curve (dashed red line). See the text for additional details.

Exercise 11.4.2

Sketch the titration curve for the titration of 50.0 mL of 0.0500 M Sn^{4+} with 0.100 M Tl^{+}. Both the titrand and the titrant are 1.0 M in HCl. The titration reaction is

$$\mathrm{Sn}^{2+}(aq)+\mathrm{Tl}^{3+}(aq) \rightarrow \mathrm{Sn}^{4+}(aq)+\mathrm{Tl}^{+}(aq) \tag{11.4.24}$$

Compare your sketch to your calculated titration curve from Practice Exercise 9.17.

Click here to review your answer to this exercise.

9.4.2 Selecting and Evaluating the End point

A redox titration's equivalence point occurs when we react stoichiometrically equivalent amounts of titrand and titrant. As is the case with acid–base and complexation titrations, we estimate the equivalence point of a complexation titration using an experimental end point. A variety of methods are available for locating the end point, including indicators and sensors that respond to a change in the solution conditions.

Where is the Equivalence Point?

For an acid–base titration or a complexometric titration the equivalence point is almost identical to the inflection point on the steeping rising part of the titration curve. If you look back at Figure 9.7 and Figure 9.28, you will see that the inflection point is in the middle of this steep rise in the titration curve, which makes it relatively easy to find the equivalence point when you sketch these titration curves. We call this a **symmetric equivalence point**. If the stoichiometry of a redox titration is symmetric—one mole of titrant reacts with each mole of titrand—then the equivalence point is symmetric. If the titration reaction's stoichiometry is not 1:1, then the equivalence point is closer to the top or to bottom of the titration curve's sharp rise. In this case we have an **asymmetric equivalence point**.

Example 11.4.1

Derive a general equation for the equivalence point's potential when titrating Fe^{2+} with MnO_4^-.

$$5\mathrm{Fe}^{2+}(aq)+\mathrm{MnO}_4^-(aq)+8\mathrm{H}^+(aq) \rightarrow 5\mathrm{Fe}^{3+}(aq)+\mathrm{Mn}^{2+}(aq)+4\mathrm{H}_2\mathrm{O} \tag{11.4.25}$$

(We often use H^+ instead of H_3O^+ when writing a redox reaction.)

Solution

The half-reactions for Fe^{2+} and MnO_4^- are

$$\mathrm{Fe}^{2+}(aq) \rightarrow \mathrm{Fe}^{3+}(aq)+e^- \tag{11.4.26}$$

$$\mathrm{MnO}_4^-(aq)+8\mathrm{H}^+(aq)+5e^- \rightarrow \mathrm{Mn}^{2+}(aq)+4\mathrm{H}_2\mathrm{O}(l) \tag{11.4.27}$$

for which the Nernst equations are

$$E=E^o_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}}-0.05916\log\frac{[\mathrm{Fe}^{2+}]}{[\mathrm{Fe}^{3+}]} \tag{11.4.28}$$

$$E=E^o_{\mathrm{MnO}_4^-/\mathrm{Mn}^{2+}}-\frac{0.05916}{5}\log\frac{[\mathrm{Mn}^{2+}]}{[\mathrm{MnO}_4^-][\mathrm{H}^+]^8} \tag{11.4.29}$$

Before adding these two equations together we must multiply the second equation by 5 so that we can combine the log terms; thus

$$6E=E^o_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}}+5E^o_{\mathrm{MnO}_4^-/\mathrm{Mn}^{2+}}-0.05916\log\frac{[\mathrm{Fe}^{2+}][\mathrm{Mn}^{2+}]}{[\mathrm{Fe}^{3+}][\mathrm{MnO}_4^-][\mathrm{H}^+]^8} \tag{11.4.30}$$

At the equivalence point we know that

$$[\mathrm{Fe}^{2+}]=5\times[\mathrm{MnO}_4^-] \tag{11.4.31}$$

$$[\mathrm{Fe}^{3+}]=5\times[\mathrm{Mn}^{2+}] \tag{11.4.32}$$

Substituting these equalities into the previous equation and rearranging gives us a general equation for the potential at the equivalence point.

$$6E_{\text{eq}}=E^o_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}}+5E^o_{\mathrm{MnO}_4^-/\mathrm{Mn}^{2+}}-0.05916\log\frac{5[\mathrm{MnO}_4^-][\mathrm{Mn}^{2+}]}{5[\mathrm{Mn}^{2+}][\mathrm{MnO}_4^-][\mathrm{H}^+]^8} \tag{11.4.33}$$

$$E_{\text{eq}}=\frac{E^o_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}}+5E^o_{\mathrm{MnO}_4^-/\mathrm{Mn}^{2+}}}{6}-\frac{0.05916}{6}\log\frac{1}{[\mathrm{H}^+]^8} \tag{11.4.34}$$

$$E_{\text{eq}}=\frac{E^o_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}}+5E^o_{\mathrm{MnO}_4^-/\mathrm{Mn}^{2+}}}{6}+\frac{0.05916\times 8}{6}\log[\mathrm{H}^+] \tag{11.4.35}$$

$$E_{\text{eq}}=\frac{E^o_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}}+5E^o_{\mathrm{MnO}_4^-/\mathrm{Mn}^{2+}}}{6}-0.07888\mathrm{pH} \tag{11.4.36}$$

Our equation for the equivalence point has two terms. The first term is a weighted average of the titrand’s and the titrant’s standard state potentials, in which the weighting factors are the number of electrons in their respective half-reactions. (Instead of standard state potentials, you can use formal potentials.) The second term shows that E_{eq} for this titration is pH-dependent. At a pH of 1 (in H_2SO_4), for example, the equivalence point has a potential of

$$E_{\text{eq}}=\frac{0.768+5\times 1.51}{6}-0.07888\times 1=1.31\text{ V} \tag{11.4.37}$$

Figure 9.38 shows a typical titration curve for titration of Fe^{2+} with MnO_4^-. Note that the titration’s equivalence point is asymmetrical.

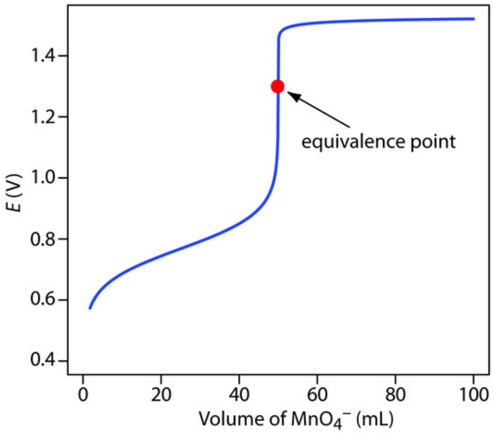


Figure 9.38: *Titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.0200 M MnO_4^- at a fixed pH of 1 (using H_2SO_4). The equivalence point is shown by the red dot.*

Exercise 11.4.3

Derive a general equation for the equivalence point’s potential for the titration of U^{4+} with Ce^{4+}. The unbalanced reaction is

$$\mathrm{Ce}^{4+}(aq)+\mathrm{U}^{4+}(aq)\rightarrow\mathrm{UO}_2^{2+}(aq)+\mathrm{Ce}^{3+}(aq) \tag{11.4.38}$$

What is the equivalence point’s potential if the pH is 1?

Click here to review your answer to this exercise.

Finding the End point with an Indicator

Three types of indicators are used to signal a redox titration's end point. The oxidized and reduced forms of some titrants, such as MnO_4^-, have different colors. A solution of MnO_4^- is intensely purple. In an acidic solution, however, permanganate's reduced form, Mn^{2+}, is nearly colorless. When using MnO_4^- as a titrant, the titrand's solution remains colorless until the equivalence point. The first drop of excess MnO_4^- produces a permanent tinge of purple, signaling the end point.

Some indicators form a colored compound with a specific oxidized or reduced form of the titrant or the titrand. Starch, for example, forms a dark blue complex with I_3^-. We can use this distinct color to signal the presence of excess I_3^- as a titrant—a change in color from colorless to blue—or the completion of a reaction consuming I_3^- as the titrand—a change in color from blue to colorless. Another example of a specific indicator is thiocyanate, SCN^-, which forms a soluble red-colored complex of $Fe(SCN)^{2+}$ with Fe^{3+}.

The most important class of indicators are substances that do not participate in the redox titration, but whose oxidized and reduced forms differ in color. When we add a **redox indicator** to the titrand, the indicator imparts a color that depends on the solution's potential. As the solution's potential changes with the addition of titrant, the indicator changes oxidation state and changes color, signaling the end point.

To understand the relationship between potential and an indicator's color, consider its reduction half-reaction

$$\mathrm{In_{ox}} + ne^- \rightleftharpoons \mathrm{In_{red}} \tag{11.4.39}$$

where $\mathrm{In_{ox}}$ and $\mathrm{In_{red}}$ are, respectively, the indicator's oxidized and reduced forms.

> *For simplicity, In_{ox} and In_{red} are shown without specific charges. Because there is a change in oxidation state, In_{ox} and In_{red} cannot both be neutral.*

The Nernst equation for this half-reaction is

$$E = E^o_{\mathrm{In_{ox}/In_{red}}} - \frac{0.05916}{n}\log\frac{[\mathrm{In_{red}}]}{[\mathrm{In_{ox}}]} \tag{11.4.40}$$

As shown in Figure 9.39, if we assume that the indicator's color changes from that of $\mathrm{In_{ox}}$ to that of $\mathrm{In_{red}}$ when the ratio $[\mathrm{In_{red}}]/[\mathrm{In_{ox}}]$ changes from 0.1 to 10, then the end point occurs when the solution's potential is within the range

$$E = E^o_{\mathrm{In_{ox}/In_{red}}} \pm \frac{0.05916}{n} \tag{11.4.41}$$

> *This is the same approach we took in considering acid–base indicators and complexation indicators.*

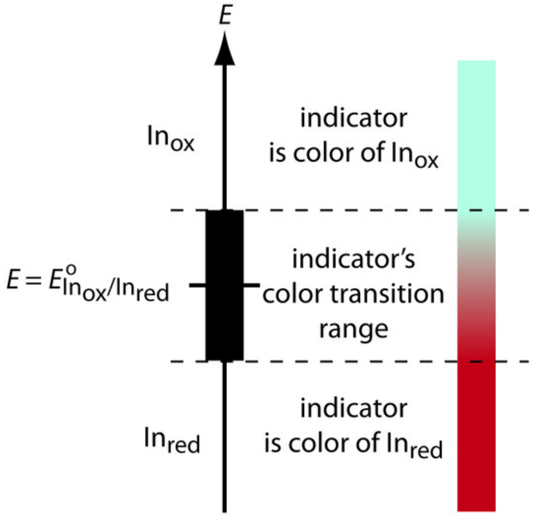


Figure 9.39 Diagram showing the relationship between E and an indicator's color. The ladder diagram defines potentials where $\mathrm{In_{red}}$ and $\mathrm{In_{ox}}$ are the predominate species. The indicator changes color when E is within the range

$$E = E^{o}_{\text{Inox/Inred}} \pm 0.05916/n$$

A partial list of redox indicators is shown in Table 9.16. Examples of appropriate and inappropriate indicators for the titration of Fe^{2+} with Ce^{4+} are shown in Figure 9.40.

Table 9.16 Selected Examples of Redox Indicators

Indicator	Color of In_{ox}	Color of In_{red}	$E^{o}In_{ox}/In_{red}$
indigo tetrasulfate	blue	colorless	0.36
methylene blue	blue	colorless	0.53
diphenylamine	violet	colorless	0.75
diphenylamine sulfonic acid	red-violet	colorless	0.85
tris(2,2´-bipyridine)iron	pale blue	red	1.120
ferroin	pale blue	red	1.147
tris(5-nitro-1,10-phenanthroline)iron	pale blue	red-violet	1.25

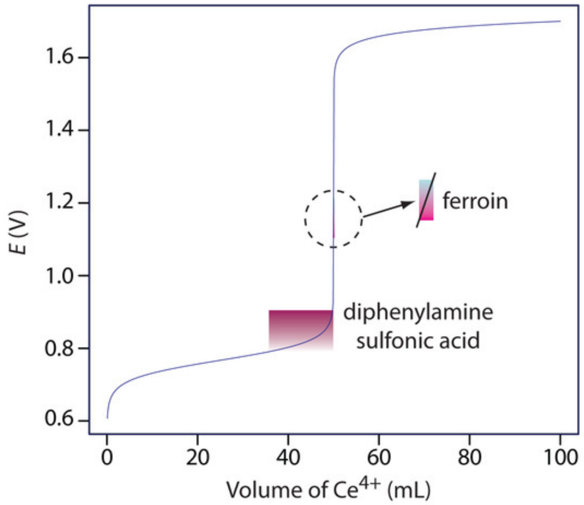


Figure 9.40: *Titration curve for the titration of 50.0 mL of 0.100 M* Fe^{2+} *with 0.100 M* Ce^{4+}*. The end point transitions for the indicators diphenylamine sulfonic acid and ferroin are superimposed on the titration curve. Because the transition for ferroin is too small to see on the scale of the x-axis—it requires only 1–2 drops of titrant—the color change is expanded to the right.*

Other Methods for Finding the End point

Another method for locating a redox titration's end point is a potentiometric titration in which we monitor the change in potential while adding the titrant to the titrand. The end point is found by visually examining the titration curve. The simplest experimental design for a potentiometric titration consists of a Pt indicator electrode whose potential is governed by the titrand's or titrant's redox half-reaction, and a reference electrode that has a fixed potential. A further discussion of potentiometry is found in Chapter 11. Other methods for locating the titration's end point include thermometric titrations and spectrophotometric titrations.

The best way to appreciate the theoretical and practical details discussed in this section is to carefully examine a typical redox titrimetric method. Although each method is unique, the following description of the determination of the total chlorine residual in water provides an instructive example of a typical procedure. The description here is based on Method 4500-Cl B as published in *Standard Methods for the Examination of Water and Wastewater*, 20th Ed., American Public Health Association: Washington, D. C., 1998.

Representative Method 9.3: **Determination of Total Chlorine Residual**

Description of the Method

The chlorination of public water supplies produces several chlorine-containing species, the combined concentration of which is called the total chlorine residual. Chlorine may be present in a variety of states, including the free residual chlorine, consisting of Cl_2, HOCl and OCl^-, and the combined chlorine residual, consisting of NH_2Cl, $NHCl_2$, and NCl_3. The total chlorine residual is determined by using the oxidizing power of chlorine to convert I^- to I_3^-. The amount of I_3^- formed is then determined by titrating with $Na_2S_2O_3$ using starch as an indicator. Regardless of its form, the total chlorine residual is reported as if Cl_2 is the only source of chlorine, and is reported as mg Cl/L.

Procedure

Select a volume of sample requiring less than 20 mL of $Na_2S_2O_3$ to reach the end point. Using glacial acetic acid, acidify the sample to a pH of 3–4, and add about 1 gram of KI. Titrate with $Na_2S_2O_3$ until the yellow color of I_3^- begins to disappear. Add 1 mL of a starch indicator solution and continue titrating until the blue color of the starch–I_3^- complex disappears (Figure 9.41). Use a blank titration to correct the volume of titrant needed to reach the end point for reagent impurities.

Questions

1. Is this an example of a direct or an indirect analysis?

This is an indirect analysis because the chlorine-containing species do not react with the titrant. Instead, the total chlorine residual oxidizes I^- to I_3^-, and the amount of I_3^- is determined by titrating with $Na_2S_2O_3$.

2. Why does the procedure rely on an indirect analysis instead of directly titrating the chlorine-containing species using KI as a titrant?

Because the total chlorine residual consists of six different species, a titration with I^- does not have a single, well-defined equivalence point. By converting the chlorine residual to an equivalent amount of I_3^-, the indirect titration with $Na_2S_2O_3$ has a single, useful equivalence point.

Even if the total chlorine residual is from a single species, such as HOCl, a direct titration with KI is impractical. Because the product of the titration, I_3^-, imparts a yellow color, the titrand's color would change with each addition of titrant, making it difficult to find a suitable indicator.

3. Both oxidizing and reducing agents can interfere with this analysis. Explain the effect of each type of interferent has on the total chlorine residual.

An interferent that is an oxidizing agent converts additional I^- to I_3^-. Because this extra I_3^- requires an additional volume of $Na_2S_2O_3$ to reach the end point, we overestimate the total chlorine residual. If the interferent is a reducing agent, it reduces back to I^- some of the I_3^- produced by the reaction between the total chlorine residual and iodide. As a result. we underestimate the total chlorine residual.

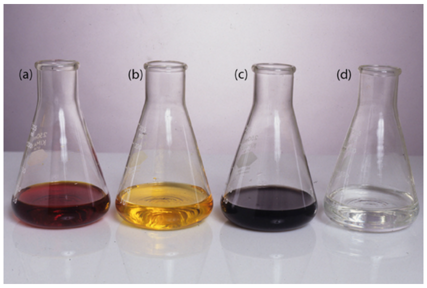


Figure 9.41 Endpoint for the determination of the total chlorine residual. (a) Acidifying the sample and adding KI forms a brown solution of I_3^-. (b) Titrating with $Na_2S_2O_3$ converts I_3^- to I^- with the solution fading to a pale yellow color as we approach the end

point. (c) Adding starch forms the deep purple starch–I_3^- complex. (d) As the titration continues, the end point is a sharp transition from a purple to a colorless solution. The change in color from (c) to (d) typically takes 1–2 drops of titrant.

9.4.3 Quantitative Applications

Although many quantitative applications of redox titrimetry have been replaced by other analytical methods, a few important applications continue to be relevant. In this section we review the general application of redox titrimetry with an emphasis on environmental, pharmaceutical, and industrial applications. We begin, however, with a brief discussion of selecting and characterizing redox titrants, and methods for controlling the titrand's oxidation state.

Adjusting the Titrand's Oxidation State

If a redox titration is to be used in a quantitative analysis, the titrand must initially be present in a single oxidation state. For example, iron can be determined by a redox titration in which Ce^{4+} oxidizes Fe^{2+} to Fe^{3+}. Depending on the sample and the method of sample preparation, iron may initially be present in both the +2 and +3 oxidation states. Before titrating, we must reduce any Fe^{3+} to Fe^{2+}. This type of pretreatment can be accomplished using an auxiliary reducing agent or oxidizing agent.

A metal that is easy to oxidize—such as Zn, Al, and Ag—can serve as an **auxiliary reducing agent**. The metal, as a coiled wire or powder, is added to the sample where it reduces the titrand. Because any unreacted auxiliary reducing agent will react with the titrant, it must be removed before beginning the titration. This can be accomplished by simply removing the coiled wire, or by filtering.

An alternative method for using an auxiliary reducing agent is to immobilize it in a column. To prepare a reduction column an aqueous slurry of the finally divided metal is packed in a glass tube equipped with a porous plug at the bottom. The sample is placed at the top of the column and moves through the column under the influence of gravity or vacuum suction. The length of the reduction column and the flow rate are selected to ensure the analyte's complete reduction.

Two common reduction columns are used. In the **Jones reductor** the column is filled with amalgamated zinc, Zn(Hg), prepared by briefly placing Zn granules in a solution of $HgCl_2$. Oxidation of zinc

$$\mathrm{Zn(Hg)}(s) \rightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Hg}(l) + 2e^- \tag{11.4.42}$$

provides the electrons for reducing the titrand. In the **Walden reductor** the column is filled with granular Ag metal. The solution containing the titrand is acidified with HCl and passed through the column where the oxidation of silver

$$\mathrm{Ag}(s) + \mathrm{Cl}^-(aq) \rightarrow \mathrm{AgCl}(s) + e^- \tag{11.4.43}$$

provides the necessary electrons for reducing the titrand. Table 9.17 provides a summary of several applications of reduction columns.

Table 9.17 Examples of Reactions For Reducing a Titrand's Oxidation State Using a Reduction Column

Oxidized Titrand	Walden Reductor	Jones Reductor
Cr^{3+}	—	$Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$
Cu^{2+}	$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	$Cu^{2+}(aq) + 2e^- \rightarrow Cr(s)$
Fe^{3+}	$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$
TiO^{2+}	—	$TiO^{2+}(aq) + 2H^+(aq) + e^- \rightarrow Ti^{3+}(aq) + H_2O(l)$
MoO_2^{2+}	$MoO_2^{2+}(aq) + e^- \rightarrow MoO_2^+(aq)$	$MoO_2^{2+}(aq) + 4H^+(aq) + 3e^- \rightarrow Mo^{3+}(aq) + 2H_2O(l)$
VO_2^+	$VO_2^+(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l)$	$VO_2^+(aq) + 4H^+(aq) + 3e^- \rightarrow V^{2+}(aq) + 2H_2O(l)$

Several reagents are commonly used as **auxiliary oxidizing agents**, including ammonium peroxydisulfate, $(NH_4)_2S_2O_8$, and hydrogen peroxide, H_2O_2. Peroxydisulfate is a powerful oxidizing agent

$$\mathrm{S_2O_8^{2-}}(aq) + 2e^- \rightarrow 2\mathrm{SO_4^{2-}}(aq) \tag{11.4.44}$$

capable of oxidizing Mn^{2+} to MnO_4^-, Cr^{3+} to $Cr_2O_7^{2-}$, and Ce^{3+} to Ce^{4+}. Excess peroxydisulfate is easily destroyed by briefly boiling the solution. The reduction of hydrogen peroxide in acidic solution

$$\mathrm{H_2O_2}(aq)+2\mathrm{H}^+(aq)+2e^- \rightarrow 2\mathrm{H_2O}(l) \tag{11.4.45}$$

provides another method for oxidizing a titrand. Excess H_2O_2 is destroyed by briefly boiling the solution.

Selecting and Standardizing a Titrant

If it is to be used quantitatively, the titrant's concentration must remain stable during the analysis. Because a titrant in a reduced state is susceptible to air oxidation, most redox titrations use an oxidizing agent as the titrant. There are several common oxidizing titrants, including MnO_4^-, Ce^{4+}, $Cr_2O_7^{2-}$, and I_3^-. Which titrant is used often depends on how easy it is to oxidize the titrand. A titrand that is a weak reducing agent needs a strong oxidizing titrant if the titration reaction is to have a suitable end point.

The two strongest oxidizing titrants are MnO_4^- and Ce^{4+}, for which the reduction half-reactions are

$$\mathrm{MnO_4^-}(aq)+8\mathrm{H}^+(aq)+5e^- \rightleftharpoons \mathrm{Mn}^{2+}(aq)+4\mathrm{H_2O}(l) \tag{11.4.46}$$

$$\mathrm{Ce}^{4+}(aq)+e^- \rightleftharpoons \mathrm{Ce}^{3+}(aq) \tag{11.4.47}$$

Solutions of Ce4+ usually are prepared from the primary standard cerium ammonium nitrate, Ce(NO3)4•2NH4NO3, in 1 M H2SO4. When prepared using a reagent grade material, such as Ce(OH)4, the solution is standardized against a primary standard reducing agent such as Na2C2O4 or Fe2+ (prepared using iron wire) using ferroin as an indicator. Despite its availability as a primary standard and its ease of preparation, Ce4+ is not as frequently used as MnO4– because it is more expensive.

Note

The standardization reactions are

$$\mathrm{Ce}^{4+}(aq)+\mathrm{Fe}^{2+}(aq) \rightarrow \mathrm{Ce}^{3+}(aq)+\mathrm{Fe}^{3+}(aq) \tag{11.4.48}$$

$$2\mathrm{Ce}^{4+}(aq)+\mathrm{H_2C_2O_4}(aq) \rightarrow 2\mathrm{Ce}^{3+}(aq)+2\mathrm{CO_2}(g)+2\mathrm{H}^+(aq) \tag{11.4.49}$$

Solutions of MnO_4^- are prepared from $KMnO_4$, which is not available as a primary standard. Aqueous solutions of permanganate are thermodynamically unstable due to its ability to oxidize water.

$$4\,\mathrm{MnO_4^-}(aq)+2\mathrm{H_2O}(l) \rightleftharpoons 4\mathrm{MnO_2}(s)+3\mathrm{O_2}(g)+4\mathrm{OH}^-(aq) \tag{11.4.50}$$

This reaction is catalyzed by the presence of MnO_2, Mn^{2+}, heat, light, and the presence of acids and bases. A moderately stable solution of permanganate can be prepared by boiling it for an hour and filtering through a sintered glass filter to remove any solid MnO_2 that precipitates. Standardization is accomplished against a primary standard reducing agent such as $Na_2C_2O_4$ or Fe^{2+} (prepared using iron wire), with the pink color of excess MnO_4^- signaling the end point. A solution of MnO_4^- prepared in this fashion is stable for 1–2 weeks, although the standardization should be rechecked periodically.

Note

The standardization reactions are

$$\mathrm{MnO_4^-}(aq)+5\mathrm{Fe}^{2+}(aq)+8\mathrm{H}^+(aq) \rightarrow \mathrm{Mn}^{2+}(aq)+5\mathrm{Fe}^{3+}(aq)+4\mathrm{H_2O}(l) \tag{11.4.51}$$

$$2\,\mathrm{MnO_4^-}(aq)+5\mathrm{H_2C_2O_4}(aq)+6\mathrm{H}^+(aq) \rightarrow 2\mathrm{Mn}^{2+}(aq)+10\mathrm{CO_2}(g)+8\mathrm{H_2O}(l) \tag{11.4.52}$$

Potassium dichromate is a relatively strong oxidizing agent whose principal advantages are its availability as a primary standard and the long term stability of its solutions. It is not, however, as strong an oxidizing agent as MnO_4^- or Ce^{4+}, which makes it less useful when the titrand is a weak reducing agent. Its reduction half-reaction is

$$\mathrm{Cr_2O_7^{2-}}(aq)+14\mathrm{H}^+(aq)+6e^- \rightleftharpoons 2\mathrm{Cr}^{3+}(aq)+7\mathrm{H_2O}(l) \tag{11.4.53}$$

Although a solution of $Cr_2O_7^{2-}$ is orange and a solution of Cr^{3+} is green, neither color is intense enough to serve as a useful indicator. Diphenylamine sulfonic acid, whose oxidized form is red-violet and reduced form is colorless, gives a very distinct end point signal with $Cr_2O_7^{2-}$.

Iodine is another important oxidizing titrant. Because it is a weaker oxidizing agent than MnO_4^-, Ce^{4+}, and $Cr_2O_7^{2-}$, it is useful only when the titrand is a stronger reducing agent. This apparent limitation, however, makes I_2 a more selective titrant for the analysis of a strong reducing agent in the presence of a weaker reducing agent. The reduction half-reaction for I_2 is

$$\mathrm{I_2}(aq) + 2e^- \rightleftharpoons 2\mathrm{I}^-(aq) \tag{11.4.54}$$

Because iodine is not very soluble in water, solutions are prepared by adding an excess of $I^–$. The complexation reaction

$$\mathrm{I_2}(aq) + \mathrm{I}^-(aq) \rightleftharpoons \mathrm{I_3^-}(aq) \tag{11.4.55}$$

increases the solubility of I_2 by forming the more soluble triiodide ion, $I_3^–$. Even though iodine is present as $I_3^–$ instead of I_2, the number of electrons in the reduction half-reaction is unaffected.

$$\mathrm{I_3^-}(aq) + 2e^- \rightleftharpoons 3\mathrm{I}^-(aq) \tag{11.4.56}$$

Solutions of $I_3^–$ are normally standardized against $Na_2S_2O_3$ using starch as a specific indicator for $I_3^–$.

Note

The standardization reaction is

$$\mathrm{I_3^-}(aq) + 2\mathrm{S_2O_3^{2-}}(aq) \rightarrow 3\mathrm{I}^-(aq) + 2\mathrm{S_4O_6^{2-}}(aq) \tag{11.4.57}$$

An oxidizing titrant such as $MnO_4^–$, Ce^{4+}, $Cr_2O_7^{2–}$, and $I_3^–$, is used when the titrand is in a reduced state. If the titrand is in an oxidized state, we can first reduce it with an auxiliary reducing agent and then complete the titration using an oxidizing titrant. Alternatively, we can titrate it using a reducing titrant. Iodide is a relatively strong reducing agent that could serve as a reducing titrant except that a solution of I– is susceptible to the air-oxidation of $I^–$ to $I_3^–$.

$$3\mathrm{I}^-(aq) \rightleftharpoons \mathrm{I_3^-}(aq) + 2e^- \tag{11.4.58}$$

Note

A freshly prepared solution of KI is clear, but after a few days it may show a faint yellow coloring due to the presence of $I_3^–$.

Instead, adding an excess of KI reduces the titrand, releasing a stoichiometric amount of $I_3^–$. The amount of $I_3^–$ produced is then determined by a back titration using thiosulfate, $S_2O_3^{2–}$, as a reducing titrant.

$$2\mathrm{S_2O_3^{2-}}(aq) \rightleftharpoons 2\mathrm{S_4O_6^{2-}}(aq) + 2e^- \tag{11.4.59}$$

Solutions of $S_2O_3^{2–}$ are prepared using $Na_2S_2O_3•5H_2O$, and must be standardized before use. Standardization is accomplished by dissolving a carefully weighed portion of the primary standard KIO_3 in an acidic solution containing an excess of KI. The reaction between $IO_3^–$ and $I^–$

$$\mathrm{IO_3^-}(aq) + 8\mathrm{I}^-(aq) + 6\mathrm{H}^+(aq) \rightarrow 3\,\mathrm{I_3^-}(aq) + 3\mathrm{H_2O}(l) \tag{11.4.60}$$

liberates a stoichiometric amount of $I_3^–$. By titrating this $I_3^–$ with thiosulfate, using starch as a visual indicator, we can determine the concentration of $S_2O_3^{2–}$ in the titrant.

Note

The standardization titration is

$$\mathrm{I_3^-}(aq) + 2\mathrm{S_2O_3^{2-}}(aq) \rightarrow 3\mathrm{I}^-(aq) + 2\mathrm{S_4O_6^{2-}}(aq) \tag{11.4.61}$$

which is the same reaction used to standardize solutions of $I_3^–$. This approach to standardizing solutions of $S_2O_3^{2–}$. is similar to the determination of the total chlorine residual outlined in Representative Method 9.3.

Although thiosulfate is one of the few reducing titrants that is not readily oxidized by contact with air, it is subject to a slow decomposition to bisulfite and elemental sulfur. If used over a period of several weeks, a solution of thiosulfate should be restandardized periodically. Several forms of bacteria are able to metabolize thiosulfate, which also can lead to a change in its concentration. This problem can be minimized by adding a preservative such as HgI_2 to the solution.

Another useful reducing titrant is ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2•6H_2O$, in which iron is present in the +2 oxidation state. A solution of Fe^{2+} is susceptible to air-oxidation, but when prepared in 0.5 M H_2SO_4 it remains stable for as long as a month. Periodic restandardization with $K_2Cr_2O_7$ is advisable. The titrant can be used to directly titrate the titrand by oxidizing Fe^{2+} to Fe^{3+}.

Alternatively, ferrous ammonium sulfate is added to the titrand in excess and the quantity of Fe^{3+} produced determined by back titrating with a standard solution of Ce^{4+} or $Cr_2O_7^{2-}$.

Inorganic Analysis

One of the most important applications of redox titrimetry is evaluating the chlorination of public water supplies. Representative Method 9.3, for example, describes an approach for determining the total chlorine residual by using the oxidizing power of chlorine to oxidize I^- to I_3^-. The amount of I_3^- is determined by back titrating with $S_2O_3^{2-}$.

The efficiency of chlorination depends on the form of the chlorinating species. There are two contributions to the total chlorine residual—the free chlorine residual and the combined chlorine residual. The free chlorine residual includes forms of chlorine that are available for disinfecting the water supply. Examples of species contributing to the free chlorine residual include Cl_2, HOCl and OCl^-. The combined chlorine residual includes those species in which chlorine is in its reduced form and, therefore, no longer capable of providing disinfection. Species contributing to the combined chlorine residual are NH_2Cl, $NHCl_2$ and NCl_3.

When a sample of iodide-free chlorinated water is mixed with an excess of the indicator *N*,*N*-diethyl-*p*-phenylenediamine (DPD), the free chlorine oxidizes a stoichiometric portion of DPD to its red-colored form. The oxidized DPD is then back titrated to its colorless form using ferrous ammonium sulfate as the titrant. The volume of titrant is proportional to the free residual chlorine.

Having determined the free chlorine residual in the water sample, a small amount of KI is added, catalyzing the reduction monochloramine, NH_2Cl, and oxidizing a portion of the DPD back to its red-colored form. Titrating the oxidized DPD with ferrous ammonium sulfate yields the amount of NH_2Cl in the sample. The amount of dichloramine and trichloramine are determined in a similar fashion.

The methods described above for determining the total, free, or combined chlorine residual also are used to establish a water supply's chlorine demand. Chlorine demand is defined as the quantity of chlorine needed to completely react with any substance that can be oxidized by chlorine, while also maintaining the desired chlorine residual. It is determined by adding progressively greater amounts of chlorine to a set of samples drawn from the water supply and determining the total, free, or combined chlorine residual.

Another important example of redox titrimetry, which finds applications in both public health and environmental analyses is the determination of dissolved oxygen. In natural waters, such as lakes and rivers, the level of dissolved O_2 is important for two reasons: it is the most readily available oxidant for the biological oxidation of inorganic and organic pollutants; and it is necessary for the support of aquatic life. In a wastewater treatment plant dissolved O_2 is essential for the aerobic oxidation of waste materials. If the concentration of dissolved O_2 falls below a critical value, aerobic bacteria are replaced by anaerobic bacteria, and the oxidation of organic waste produces undesirable gases, such as CH_4 and H_2S.

One standard method for determining the dissolved O_2 content of natural waters and wastewaters is the Winkler method. A sample of water is collected without exposing it to the atmosphere, which might change the concentration of dissolved O_2. The sample is first treated with a solution of $MnSO_4$, and then with a solution of NaOH and KI. Under these alkaline conditions the dissolved oxygen oxidizes Mn^{2+} to MnO_2.

$$2\mathrm{Mn}^{2+}(aq)+4\mathrm{OH}^{-}(aq)+\mathrm{O}_2(g)\rightarrow 2\mathrm{MnO}_2(s)+2\mathrm{H}_2\mathrm{O}(l) \tag{11.4.62}$$

After the reaction is complete, the solution is acidified with H_2SO_4. Under the now acidic conditions I^- is oxidized to I_3^- by MnO_2.

$$\mathrm{MnO}_2(s)+3\mathrm{I}^{-}(aq)+4\mathrm{H}^{+}(aq)\rightarrow \mathrm{Mn}^{2+}+\mathrm{I}_3^{-}(aq)+2\mathrm{H}_2\mathrm{O}(l) \tag{11.4.63}$$

The amount of I_3^- formed is determined by titrating with $S_2O_3^{2-}$ using starch as an indicator. The Winkler method is subject to a variety of interferences, and several modifications to the original procedure have been proposed. For example, NO_2^- interferes because it can reduce I_3^- to I^- under acidic conditions. This interference is eliminated by adding sodium azide, NaN_3, reducing NO_2^- to N_2. Other reducing agents, such as Fe^{2+}, are eliminated by pretreating the sample with $KMnO_4$, and destroying the excess permanganate with $K_2C_2O_4$.

Another important example of redox titrimetry is the determination of water in nonaqueous solvents. The titrant for this analysis is known as the Karl Fischer reagent and consists of a mixture of iodine, sulfur dioxide, pyridine, and methanol. Because the concentration of pyridine is sufficiently large, I_2 and SO_2 react with pyridine (py) to form the complexes py•I_2 and py•SO_2. When added to a sample containing water, I_2 is reduced to I^- and SO_2 is oxidized to SO_3.

$$\mathrm{py}\bullet\mathrm{I}_2+\mathrm{py}\bullet\mathrm{SO}_2+\mathrm{py}+\mathrm{H}_2\mathrm{O}\rightarrow 2\mathrm{py}\bullet\mathrm{HI}+\mathrm{py}\bullet\mathrm{SO}_3 \tag{11.4.64}$$

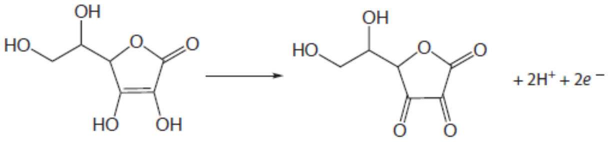
Methanol is included to prevent the further reaction of py•SO_3 with water. The titration's end point is signaled when the solution changes from the product's yellow color to the brown color of the Karl Fischer reagent.

Organic Analysis

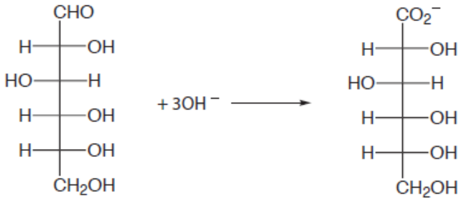
Redox titrimetry also is used for the analysis of organic analytes. One important example is the determination of the chemical oxygen demand (COD) of natural waters and wastewaters. The COD provides a measure of the quantity of oxygen necessary to completely oxidize all the organic matter in a sample to CO_2 and H_2O. Because no attempt is made to correct for organic matter that can not be decomposed biologically, or for slow decomposition kinetics, the COD always overestimates a sample's true oxygen demand. The determination of COD is particularly important in managing industrial wastewater treatment facilities where it is used to monitor the release of organic-rich wastes into municipal sewer systems or the environment.

A sample's COD is determined by refluxing it in the presence of excess $K_2Cr_2O_7$, which serves as the oxidizing agent. The solution is acidified with H_2SO_4 using Ag_2SO_4 to catalyze the oxidation of low molecular weight fatty acids. Mercuric sulfate, $HgSO_4$, is added to complex any chloride that is present, preventing the precipitation of the Ag^+ catalyst as AgCl. Under these conditions, the efficiency for oxidizing organic matter is 95–100%. After refluxing for two hours, the solution is cooled to room temperature and the excess $Cr_2O_7^{2-}$ is determined by back titrating using ferrous ammonium sulfate as the titrant and ferroin as the indicator. Because it is difficult to completely remove all traces of organic matter from the reagents, a blank titration must be performed. The difference in the amount of ferrous ammonium sulfate needed to titrate the sample and the blank is proportional to the COD.

Iodine has been used as an oxidizing titrant for a number of compounds of pharmaceutical interest. Earlier we noted that the reaction of $S_2O_3^{2-}$ with I_3^- produces the tetrathionate ion, $S_4O_6^{2-}$. The tetrathionate ion is actually a dimer consisting of two thiosulfate ions connected through a disulfide (–S–S–) linkage. In the same fashion, I_3^- can be used to titrate mercaptans of the general formula RSH, forming the dimer RSSR as a product. The amino acid cysteine also can be titrated with I_3^-. The product of this titration is cystine, which is a dimer of cysteine. Triiodide also can be used for the analysis of ascorbic acid (vitamin C) by oxidizing the enediol functional group to an alpha diketone



and for the analysis of reducing sugars, such as glucose, by oxidizing the aldehyde functional group to a carboxylate ion in a basic solution.



An organic compound containing a hydroxyl, a carbonyl, or an amine functional group adjacent to an hydoxyl or a carbonyl group can be oxidized using metaperiodate, IO_4^-, as an oxidizing titrant.

$$\mathrm{IO_4^-}(aq) + \mathrm{H_2O}(l) + 2e^- \rightleftharpoons \mathrm{IO_3^-}(aq) + 2\mathrm{OH}^-(aq) \tag{11.4.65}$$

A two-electron oxidation cleaves the C–C bond between the two functional groups, with hydroxyl groups being oxidized to aldehydes or ketones, carbonyl functional groups being oxidized to carboxylic acids, and amines being oxidized to an aldehyde and an amine (ammonia if a primary amine). The analysis is conducted by adding a known excess of IO_4^- to the solution containing the analyte, and allowing the oxidation to take place for approximately one hour at room temperature. When the oxidation is complete, an excess of KI is added, which converts any unreacted IO_4^- to IO_3^- and I_3^-.

$$\mathrm{IO_4^-}(aq) + 3\mathrm{I}^-(aq) + \mathrm{H_2O}(l) \rightarrow \mathrm{IO_3^-}(aq) + \mathrm{I_3^-}(aq) + 2\mathrm{OH}^-(aq) \tag{11.4.66}$$

The I_3^- is then determined by titrating with $S_2O_3^{2-}$ using starch as an indicator.

Quantitative Calculations

The quantitative relationship between the titrand and the titrant is determined by the stoichiometry of the titration reaction. If you are unsure of the balanced reaction, you can deduce the stoichiometry by remembering that the electrons in a redox reaction must be conserved.

Example 9.11

The amount of Fe in a 0.4891-g sample of an ore was determined by titrating with $K_2Cr_2O_7$. After dissolving the sample in HCl, the iron was brought into the +2 oxidation state using a Jones reductor. Titration to the diphenylamine sulfonic acid end point required 36.92 mL of 0.02153 M $K_2Cr_2O_7$. Report the ore's iron content as %w/w Fe_2O_3.

(Although we can deduce the stoichiometry between the titrant and the titrand without balancing the titration reaction, the balanced reaction

$$\mathrm{K_2Cr_2O_7}(aq) + 6\mathrm{Fe}^{2+}(aq) + 14\mathrm{H}^+(aq) \rightarrow 2\mathrm{Cr}^{3+}(aq) + 2\mathrm{K}^+(aq) + 6\mathrm{Fe}^{3+}(aq) + 7\mathrm{H_2O}(l) \tag{11.4.67}$$

does provide useful information. For example, the presence of H^+ reminds us that the reaction^fs feasibility is pH-dependent.)

Solution

Because we have not been provided with the titration reaction, let's use a conservation of electrons to deduce the stoichiometry. During the titration the analyte is oxidized from Fe^{2+} to Fe^{3+}, and the titrant is reduced from $Cr_2O_7^{2-}$ to Cr^{3+}. Oxidizing Fe^{2+} to Fe^{3+} requires only a single electron. Reducing $Cr_2O_7^{2-}$, in which each chromium is in the +6 oxidation state, to Cr^{3+} requires three electrons per chromium, for a total of six electrons. A conservation of electrons for the titration, therefore, requires that each mole of $K_2Cr_2O_7$ reacts with six moles of Fe^{2+}.

The moles of $K_2Cr_2O_7$ used in reaching the end point is

$$(0.02153 \text{ M } \mathrm{K_2Cr_2O_7}) \times (0.03692 \text{ L } \mathrm{K_2Cr_2O_7}) = 7.949 \times 10^{-4} \text{ mol } \mathrm{K_2Cr_2O_7} \tag{11.4.68}$$

which means that the sample contains

$$7.949 \times 10^{-4} \text{ mol } \mathrm{K_2Cr_2O_7} \times \frac{6 \text{ mol } \mathrm{Fe}^{2+}}{\text{mol } \mathrm{K_2Cr_2O_7}} = 4.769 \times 10^{-3} \text{ mol } \mathrm{Fe}^{2+} \tag{11.4.69}$$

Thus, the %w/w Fe_2O_3 in the sample of ore is

$$4.769 \times 10^{-3} \text{ mol } \mathrm{Fe}^{2+} \times \frac{1 \text{ mol } \mathrm{Fe_2O_3}}{2 \text{ mol } \mathrm{Fe}^{2+}} \times \frac{159.69 \text{ g } \mathrm{Fe_2O_3}}{\text{mol } \mathrm{Fe_2O_3}} = 0.3808 \text{ g } \mathrm{Fe_2O_3} \tag{11.4.70}$$

$$\frac{0.3808 \text{ g } \mathrm{Fe_2O_3}}{0.4891 \text{ g sample}} \times 100 = 77.86\% \text{ w/w } \mathrm{Fe_2O_3} \tag{11.4.71}$$

Practice Exercise 9.20

The purity of a sample of sodium oxalate, $Na_2C_2O_4$, is determined by titrating with a standard solution of $KMnO_4$. If a 0.5116-g sample requires 35.62 mL of 0.0400 M $KMnO_4$ to reach the titration's end point, what is the %w/w $Na_2C_2O_4$ in the sample.

Click here to review your answer to this exercise.

As shown in the following two examples, we can easily extend this approach to an analysis that requires an indirect analysis or a back titration.

Example 9.12

A 25.00-mL sample of a liquid bleach was diluted to 1000 mL in a volumetric flask. A 25-mL portion of the diluted sample was transferred by pipet into an Erlenmeyer flask containing an excess of KI, reducing the OCl^- to Cl^-, and producing I_3^-. The liberated I_3^- was determined by titrating with 0.09892 M $Na_2S_2O_3$, requiring 8.96 mL to reach the starch indicator end point. Report the %w/v NaOCl in the sample of bleach.

Solution

To determine the stoichiometry between the analyte, NaOCl, and the titrant, $Na_2S_2O_3$, we need to consider both the reaction between OCl^- and I^-, and the titration of I_3^- with $Na_2S_2O_3$.

First, in reducing $OCl^–$ to $Cl^–$, the oxidation state of chlorine changes from +1 to –1, requiring two electrons. The oxidation of three $I^–$ to form $I_3^–$ releases two electrons as the oxidation state of each iodine changes from –1 in $I^–$ to –⅓ in $I_3^–$. A conservation of electrons, therefore, requires that each mole of $OCl^–$ produces one mole of $I_3^–$.

Second, in the titration reaction, $I_3^–$. is reduced to $I^–$ and $S_2O_3^{2–}$ is oxidized to $S_4O_6^{2–}$. Reducing $I_3^–$ to $3I^–$ requires two elections as each iodine changes from an oxidation state of –⅓ to –1. In oxidizing $S_2O_3^{2–}$ to $S_4O_6^{2–}$, each sulfur changes its oxidation state from +2 to +2.5, releasing one electron for each $S_2O_3^{2–}$. A conservation of electrons, therefore, requires that each mole of $I_3^–$ reacts with two moles of $S_2O_3^{2–}$.

Finally, because each mole of $OCl^–$ produces one mole of $I_3^–$, and each mole of $I_3^–$ reacts with two moles of $S_2O_3^{2–}$, we know that every mole of NaOCl in the sample ultimately results in the consumption of two moles of $Na_2S_2O_3$.

The balanced reactions for this analysis are:

$$\mathrm{OCl^-}(aq) + 3\mathrm{I^-}(aq) + 2\mathrm{H^+}(aq) \rightarrow \mathrm{I_3^-}(aq) + \mathrm{Cl^-}(aq) + \mathrm{H_2O}(l) \tag{11.4.72}$$

$$\mathrm{I_3^-}(aq) + 2\mathrm{S_2O_3^{2-}}(aq) \rightarrow \mathrm{S_4O_6^{2-}}(aq) + 3\mathrm{I^-}(aq) \tag{11.4.73}$$

The moles of $Na_2S_2O_3$ used in reaching the titration's end point is

$$(0.09892 \text{ M Na}_2\text{S}_2\text{O}_3) \times (0.00896 \text{ L Na}_2\text{S}_2\text{O}_3) = 8.86 \times 10^{-4} \text{ mol Na}_2\text{S}_2\text{O}_3 \tag{11.4.74}$$

which means the sample contains

$$8.86 \times 10^{-4} \text{ mol Na}_2\text{S}_2\text{O}_3 \times \frac{1 \text{ mol NaOCl}}{2 \text{ mol Na}_2\text{S}_2\text{O}_3} \times \frac{74.44 \text{ g NaOCl}}{\text{mol NaOCl}} = 0.03299 \text{ g NaOCl} \tag{11.4.75}$$

Thus, the %w/v NaOCl in the diluted sample is

$$\frac{0.03299 \text{ g NaOCl}}{25.00 \text{ mL}} \times 100 = 0.132\% \text{ w/v NaOCl} \tag{11.4.76}$$

Because the bleach was diluted by a factor of 40 (25 mL to 1000 mL), the concentration of NaOCl in the bleach is 5.28% (w/v).

Example 9.13

The amount of ascorbic acid, $C_6H_8O_6$, in orange juice was determined by oxidizing the ascorbic acid to dehydroascorbic acid, $C_6H_6O_6$, with a known amount of $I_3^–$, and back titrating the excess $I_3^–$ with $Na_2S_2O_3$. A 5.00-mL sample of filtered orange juice was treated with 50.00 mL of 0.01023 M $I_3^–$. After the oxidation was complete, 13.82 mL of 0.07203 M $Na_2S_2O_3$ was needed to reach the starch indicator end point. Report the concentration ascorbic acid in mg/100 mL.

Solution

For a back titration we need to determine the stoichiometry between $I_3^–$ and the analyte, $C_6H_8O_6$, and between $I_3^–$ and the titrant, $Na_2S_2O_3$. The later is easy because we know from Example 9.12 that each mole of $I_3^–$ reacts with two moles of $Na_2S_2O_3$.

The balanced reactions for this analysis are:

$$\mathrm{C_6H_8O_6}(aq) + \mathrm{I_3^-}(aq) \rightarrow 3\mathrm{I^-}(aq) + \mathrm{C_6H_6O_6}(aq) + 2\mathrm{H^+}(aq) \tag{11.4.77}$$

$$\mathrm{I_3^-}(aq) + 2\mathrm{S_2O_3^{2-}}(aq) \rightarrow \mathrm{S_4O_6^{2-}}(aq) + 3\mathrm{I^-}(aq) \tag{11.4.78}$$

In oxidizing ascorbic acid to dehydroascorbic acid, the oxidation state of carbon changes from +⅔ in $C_6H_8O_6$ to +1 in $C_6H_6O_6$. Each carbon releases ⅓ of an electron, or a total of two electrons per ascorbic acid. As we learned in Example 9.12, reducing $I_3^–$ requires two electrons; thus, a conservation of electrons requires that each mole of ascorbic acid consumes one mole of $I_3^–$.

The total moles of $I_3^–$ reacting with $C_6H_8O_6$ and with $Na_2S_2O_3$ is

$$(0.01023 \text{ M I}_3^-) \times (0.05000 \text{ L I}_3^-) = 5.115 \times 10^{-4} \text{ mol I}_3^- \tag{11.4.79}$$

The back titration consumes

$$0.01382 \text{ L Na}_2\text{S}_2\text{O}_3 \times \frac{0.07203 \text{ mol Na}_2\text{S}_2\text{O}_3}{\text{L Na}_2\text{S}_2\text{O}_3} \times \frac{1 \text{ mol I}_3^-}{2 \text{ mol Na}_2\text{S}_2\text{O}_3} = 4.977 \times 10^{-4} \text{ mol I}_3^- \tag{11.4.80}$$

Subtracting the moles of $I_3^–$ reacting with $Na_2S_2O_3$ from the total moles of $I_3^–$ gives the moles reacting with ascorbic acid.

$$5.115 \times 10^{-4} \text{ mol } \text{I}_3^- - 4.977 \times 10^{-4} \text{ mol } \text{I}_3^- = 1.38 \times 10^{-5} \text{ mol } \text{I}_3^- \tag{11.4.81}$$

The grams of ascorbic acid in the 5.00-mL sample of orange juice is

$$1.38 \times 10^{-5} \text{ mol } \text{I}_3^- \times \frac{1 \text{ mol } \text{C}_6\text{H}_8\text{O}_6}{\text{mol } \text{I}_3^-} \times \frac{176.13 \text{ g } \text{C}_6\text{H}_8\text{O}_6}{\text{mol } \text{C}_6\text{H}_8\text{O}_6} = 2.43 \times 10^{-3} \text{ g } \text{C}_6\text{H}_8\text{O}_6 \tag{11.4.82}$$

There are 2.43 mg of ascorbic acid in the 5.00-mL sample, or 48.6 mg per 100 mL of orange juice.

Practice Exercise 9.21

A quantitative analysis for ethanol, C_2H_6O, can be accomplished by a redox back titration. Ethanol is oxidized to acetic acid, $C_2H_4O_2$, using excess dichromate, $Cr_2O_7^{2-}$, which is reduced to Cr^{3+}. The excess dichromate is titrated with Fe^{2+}, giving Cr^{3+} and Fe^{3+} as products. In a typical analysis, a 5.00-mL sample of a brandy is diluted to 500 mL in a volumetric flask. A 10.00-mL sample is taken and the ethanol is removed by distillation and collected in 50.00 mL of an acidified solution of 0.0200 M $K_2Cr_2O_7$. A back titration of the unreacted $Cr_2O_7^{2-}$ requires 21.48 mL of 0.1014 M Fe^{2+}. Calculate the %w/v ethanol in the brandy.

Click here to review your answer to this exercise.

9.4.4 Evaluation of Redox Titrimetry

The scale of operations, accuracy, precision, sensitivity, time, and cost of a redox titration are similar to those described earlier in this chapter for acid–base or a complexation titration. As with acid–base titrations, we can extend a redox titration to the analysis of a mixture of analytes if there is a significant difference in their oxidation or reduction potentials. Figure 9.42 shows an example of the titration curve for a mixture of Fe^{2+} and Sn^{2+} using Ce^{4+} as the titrant. A titration of a mixture of analytes is possible if their standard state potentials or formal potentials differ by at least 200 mV.

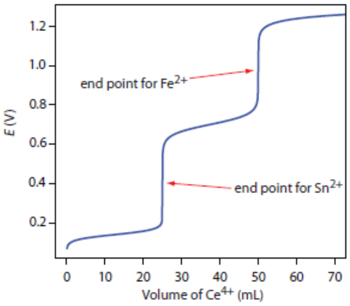


Figure 9.42 *Titration curve for the titration of 50.0 mL of 0.0125 M Sn^{2+} and 0.0250 M Fe^{2+} with 0.050 M Ce^{4+}. Both the titrand and the titrant are 1M in HCl.*

Contributors

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11.5: Phase Equilibrium in Solutions - Nonvolatile Solutes

Learning Objectives

- To describe the relationship between solute concentration and the physical properties of a solution.
- To understand that the total number of nonvolatile solute particles determines the decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus the pure solvent.

Many of the physical properties of solutions differ significantly from those of the pure substances discussed in earlier chapters, and these differences have important consequences. For example, the limited temperature range of liquid water (0°C–100°C) severely limits its use. Aqueous solutions have both a lower freezing point and a higher boiling point than pure water. Probably one of the most familiar applications of this phenomenon is the addition of ethylene glycol (“antifreeze”) to the water in an automobile radiator. This solute lowers the freezing point of the water, preventing the engine from cracking in very cold weather from the expansion of pure water on freezing. Antifreeze also enables the cooling system to operate at temperatures greater than 100°C without generating enough pressure to explode.

Changes in the freezing point and boiling point of a solution depend primarily on the number of solute particles present rather than the kind of particles. Such properties of solutions are called colligative properties (from the Latin *colligatus*, meaning “bound together” as in a quantity). As we will see, the vapor pressure and osmotic pressure of solutions are also colligative properties.

Counting Concentrations and Effective Concentrations

When we determine the number of particles in a solution, it is important to remember that not all solutions with the same molarity contain the same concentration of solute particles. Consider, for example, 0.01 M aqueous solutions of sucrose, NaCl, and $\mathrm{CaCl_2}$. Because sucrose dissolves to give a solution of neutral molecules, the concentration of solute particles in a 0.01 M sucrose solution is 0.01 M. In contrast, both NaCl and $\mathrm{CaCl_2}$ are ionic compounds that dissociate in water to yield solvated ions. As a result, a 0.01 M aqueous solution of NaCl contains 0.01 M $\mathrm{Na^+}$ ions and 0.01 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.02 M. Similarly, the $\mathrm{CaCl_2}$ solution contains 0.01 M $\mathrm{Ca^{2+}}$ ions and 0.02 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.03 M. These values are correct for dilute solutions, where the dissociation of the compounds to form separately solvated ions is complete.

At **higher concentrations** (typically >1 M), especially with salts of small, highly charged ions (such as $\mathrm{Mg^{2+}}$ or $\mathrm{Al^{3+}}$), or in solutions with less polar solvents, dissociation to give separate ions is often incomplete. The sum of the concentrations of the dissolved solute particles dictates the physical properties of a solution. In the following discussion, we must therefore keep the chemical nature of the solute firmly in mind. A greater discussion of this is below.

Vapor Pressure of Solutions and Raoult’s Law For Nonvolatile Solutes

Adding a nonvolatile solute, one whose vapor pressure is too low to measure readily, to a volatile solvent decreases the vapor pressure of the solvent. We can understand this phenomenon qualitatively by examining Figure $11.5.1$, which is a schematic diagram of the surface of a solution of glucose in water. In an aqueous solution of glucose, a portion of the surface area is occupied by nonvolatile glucose molecules rather than by volatile water molecules. As a result, fewer water molecules can enter the vapor phase per unit time, even though the surface water molecules have the same kinetic energy distribution as they would in pure water. At the same time, the rate at which water molecules in the vapor phase collide with the surface and reenter the solution is unaffected. The net effect is to shift the dynamic equilibrium between water in the vapor and the liquid phases, decreasing the vapor pressure of the solution compared with the vapor pressure of the pure solvent.

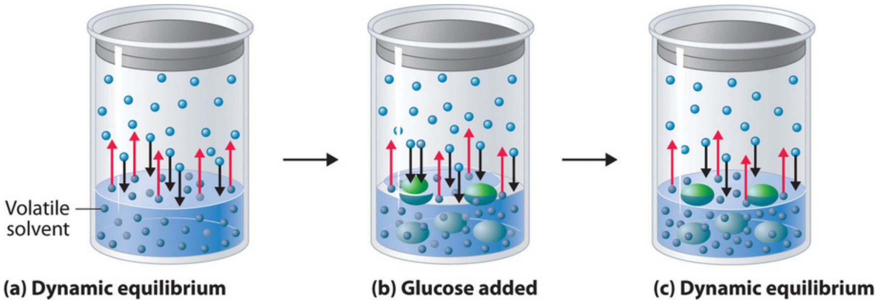


Figure 11.5.1: A Model Depicting Why the Vapor Pressure of a Solution of Glucose Is Less Than the Vapor Pressure of Pure Water. (a) When water or any volatile solvent is in a closed container, water molecules move into and out of the liquid phase at the same rate in a dynamic equilibrium. (b) If a nonvolatile solute such as glucose is added, some fraction of the surface area is occupied by solvated solute molecules. As a result, the rate at which water molecules evaporate is decreased, although initially their rate of condensation is unchanged. (c) When the glucose solution reaches equilibrium, the concentration of water molecules in the vapor phase, and hence the vapor pressure, is less than that of pure water. (CC BY-NC-SA; anonymous)

Figure $11.5.2$ shows two beakers, one containing pure water and one containing an aqueous glucose solution, in a sealed chamber. We can view the system as having two competing equilibria: water vapor will condense in both beakers at the same rate, but water molecules will evaporate more slowly from the glucose solution because fewer water molecules are at the surface. Eventually all of the water will evaporate from the beaker containing the liquid with the higher vapor pressure (pure water) and condense in the beaker containing the liquid with the lower vapor pressure (the glucose solution). If the system consisted of only a beaker of water inside a sealed container, equilibrium between the liquid and vapor would be achieved rather rapidly, and the amount of liquid water in the beaker would remain constant.

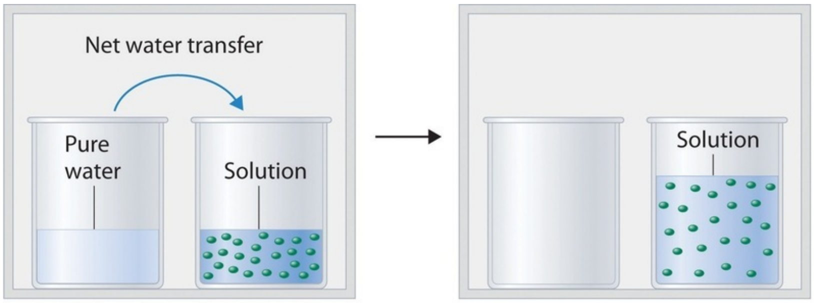


Figure 11.5.2: Transfer of Water to a Beaker Containing a Glucose Solution. (top) One beaker contains an aqueous solution of glucose, and the other contains pure water. If they are placed in a sealed chamber, the lower vapor pressure of water in the glucose solution results in a net transfer of water from the beaker containing pure water to the beaker containing the glucose solution. (bottom) Eventually, all of the water is transferred to the beaker that has the glucose solution. (CC BY-NC-SA; anonymous)

If the particles of a solute are essentially the same size as those of the solvent and both solute and solvent have roughly equal probabilities of being at the surface of the solution, then the effect of a solute on the vapor pressure of the solvent is proportional to the number of sites occupied by solute particles at the surface of the solution. Doubling the concentration of a given solute causes twice as many surface sites to be occupied by solute molecules, resulting in twice the decrease in vapor pressure. The relationship between solution composition and vapor pressure is therefore

$$P_A = \chi_A P_A^0 \tag{11.5.1}$$

where P_A is the vapor pressure of component A of the solution (in this case the solvent), χ_A is the mole fraction of A in solution, and P_A^0 is the vapor pressure of pure A. Equation 11.5.1 is known as **Raoult’s law**, after the French chemist who developed it. If the solution contains only a single nonvolatile solute (B), then we can relate the mole fraction of the solvent to the solute

$$\chi_A + \chi_B = 1$$

and we can substitute $\chi_A = 1 - \chi_B$ into Equation 11.5.1 to obtain

$$\begin{aligned} P_A &= (1-\chi_B)P_A^0 \\ &= P_A^0 - \chi_B P_A^0 \end{aligned}$$

Rearranging and defining $\Delta P_A = P_A^0 - P_A$, we obtain a relationship between the decrease in vapor pressure and the mole fraction of nonvolatile solute:

$$P_A^0 - P_A = \Delta P_A \tag{11.5.2}$$

$$= \chi_B P_A^0 \tag{11.5.3}$$

We can solve vapor pressure problems in either of two ways: by using Equation 11.5.1 to calculate the actual vapor pressure above a solution of a nonvolatile solute, or by using Equation 11.5.3 to calculate the decrease in vapor pressure caused by a specified amount of a nonvolatile solute.

✓ Example 11.5.1: Anti-Freeze

Ethylene glycol ($HOCH_2CH_2OH$), the major ingredient in commercial automotive antifreeze, increases the boiling point of radiator fluid by lowering its vapor pressure. At 100°C, the vapor pressure of pure water is 760 mmHg. Calculate the vapor pressure of an aqueous solution containing 30.2% ethylene glycol by mass, a concentration commonly used in climates that do not get extremely cold in winter.

Given: identity of solute, percentage by mass, and vapor pressure of pure solvent

Asked for: vapor pressure of solution

Strategy:

A. Calculate the number of moles of ethylene glycol in an arbitrary quantity of water, and then calculate the mole fraction of water.
B. Use Raoult's law (Equation 11.5.1) to calculate the vapor pressure of the solution.

Solution:

A A 30.2% solution of ethylene glycol contains 302 g of ethylene glycol per kilogram of solution; the remainder (698 g) is water. To use Raoult's law to calculate the vapor pressure of the solution, we must know the mole fraction of water. Thus we must first calculate the number of moles of both ethylene glycol (EG) and water present:

$$moles\ EG = (302\ \cancel{g})\left(\frac{1\ mol}{62.07\ \cancel{g}}\right) = 4.87\ mol\ EG$$

$$moles\ H_2O = (698\ \cancel{g})\left(\frac{1\ mol}{18.02\ \cancel{g}}\right) = 38.7\ mol\ H_2O$$

The mole fraction of water is thus

$$\chi_{H_2O} = \frac{38.7\ \cancel{mol}\ H_2O}{38.7\ \cancel{mol}\ H_2O + 4.87\ \cancel{mol}\ EG} = 0.888$$

B From Raoult's law (Equation 11.5.1), the vapor pressure of the solution is

$$\begin{aligned} P_{H_2O} &= (\chi_{H_2O})(P^0_{H_2O}) \\ &= (0.888)(760\ mmHg) = 675\ mmHg \end{aligned}$$

Alternatively, we could solve this problem by calculating the mole fraction of ethylene glycol and then using Equation 11.5.3 to calculate the resulting decrease in vapor pressure:

$$\begin{aligned} \chi_{EG} &= \frac{4.87\ mol\ EG}{4.87\ mol\ EG + 38.7\ mol\ H_2O} \\ &= 0.112 \end{aligned}$$

$$\begin{aligned} \Delta P_{H_2O} &= (\chi_{EG})(P^0_{H_2O}) \\ &= (0.112)(760\ mmHg) = 85.1\ mmHg \end{aligned}$$

$$P_{H_2O} = P^0_{H_2O} - \Delta P_{H_2O} = 760\ mmHg - 85.1\ mmHg = 675\ mmHg$$

The same result is obtained using either method.

? Exercise 11.5.1

Seawater is an approximately 3.0% aqueous solution of NaCl by mass with about 0.5% of other salts by mass. Calculate the decrease in the vapor pressure of water at 25°C caused by this concentration of NaCl, remembering that 1 mol of NaCl produces 2 mol of solute particles. The vapor pressure of pure water at 25°C is 23.8 mmHg.

Answer

0.45 mmHg. This may seem like a small amount, but it constitutes about a 2% decrease in the vapor pressure of water and accounts in part for the higher humidity in the north-central United States near the Great Lakes, which are freshwater lakes. The decrease therefore has important implications for climate modeling.

Boiling Point Elevation

Recall that the normal boiling point of a substance is the temperature at which the vapor pressure equals 1 atm. If a nonvolatile solute lowers the vapor pressure of a solvent, it must also affect the boiling point. Because the vapor pressure of the solution at a given temperature is less than the vapor pressure of the pure solvent, achieving a vapor pressure of 1 atm for the solution requires a higher temperature than the normal boiling point of the solvent. Thus the boiling point of a solution is always greater than that of the pure solvent. We can see why this must be true by comparing the phase diagram for an aqueous solution with the phase diagram for pure water (Figure 11.5.4). The vapor pressure of the solution is less than that of pure water at all temperatures. Consequently, the liquid–vapor curve for the solution crosses the horizontal line corresponding to $P = 1\,atm$ at a higher temperature than does the curve for pure water.

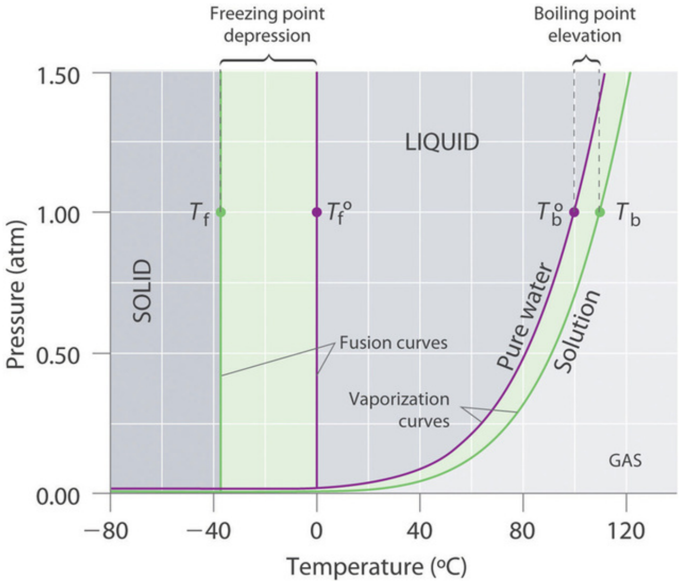


Figure 11.5.4: Phase Diagrams of Pure Water and an Aqueous Solution of a Nonvolatile Solute. The vaporization curve for the solution lies below the curve for pure water at all temperatures, which results in an increase in the boiling point and a decrease in the freezing point of the solution. (CC BY-NC-SA; anonymous)

> *The boiling point of a solution with a nonvolatile solute is* ***always*** *greater than the boiling point of the pure solvent.*

The magnitude of the increase in the boiling point is related to the magnitude of the decrease in the vapor pressure. As we have just discussed, the decrease in the vapor pressure is proportional to the concentration of the solute in the solution. Hence the magnitude of the increase in the boiling point must also be proportional to the concentration of the solute (Figure 11.5.5).

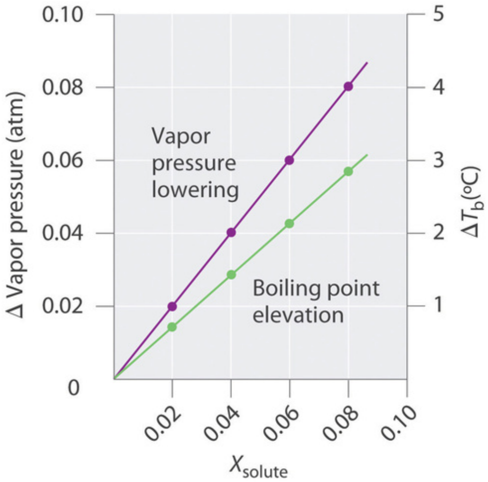


Figure 11.5.5: Vapor Pressure Decrease and Boiling Point Increase as Functions of the Mole Fraction of a Nonvolatile Solute. (CC BY-NC-SA; anonymous)

We can define the boiling point elevation (ΔT_b) as the difference between the boiling points of the solution and the pure solvent:

$$\Delta T_b = T_b - T_b^0 \tag{11.5.4}$$

where T_b is the boiling point of the solution and T_b^0 is the boiling point of the pure solvent. We can express the relationship between ΔT_b and concentration as follows

$$\Delta T_b = mK_b \tag{11.5.5}$$

where m is the concentration of the solute expressed in molality, and K_b is the **molal boiling point elevation constant** of the solvent, which has units of °C/m. Table $11.5.1$ lists characteristic K_b values for several commonly used solvents. For relatively dilute solutions, the magnitude of both properties is proportional to the solute concentration.

Table 11.5.1: Boiling Point Elevation Constants (K_b) and Freezing Point Depression Constants (K_f) for Some Solvents

Solvent	Boiling Point (°C)	K_b (°C/m)	Freezing Point (°C)	K_f (°C/m)
acetic acid	117.90	3.22	16.64	3.63
benzene	80.09	2.64	5.49	5.07
d-(+)-camphor	207.4	4.91	178.8	37.8
carbon disulfide	46.2	2.42	−112.1	3.74
carbon tetrachloride	76.8	5.26	−22.62	31.4
chloroform	61.17	3.80	−63.41	4.60
nitrobenzene	210.8	5.24	5.70	6.87
water	100.00	0.51	0.00	1.86

The concentration of the solute is typically expressed as molality rather than mole fraction or molarity for two reasons. First, because the density of a solution changes with temperature, the value of molarity also varies with temperature. If the boiling point depends on the solute concentration, then by definition the system is not maintained at a constant temperature. Second, molality and mole fraction are proportional for relatively dilute solutions, but molality has a larger numerical value (a mole fraction can be only between zero and one). Using molality allows us to eliminate nonsignificant zeros.

According to Table $11.5.1$, the molal boiling point elevation constant for water is 0.51°C/m. Thus a 1.00 m aqueous solution of a nonvolatile molecular solute such as glucose or sucrose will have an increase in boiling point of 0.51°C, to give a boiling point of 100.51°C at 1.00 atm. The increase in the boiling point of a 1.00 m aqueous NaCl solution will be approximately twice as large as that of the glucose or sucrose solution because 1 mol of NaCl produces 2 mol of dissolved ions. Hence a 1.00 m NaCl solution will have a boiling point of about 101.02°C.

✓ Example 11.5.3

In Example 11.5.1, we calculated that the vapor pressure of a 30.2% aqueous solution of ethylene glycol at 100°C is 85.1 mmHg less than the vapor pressure of pure water. We stated (without offering proof) that this should result in a higher boiling point for the solution compared with pure water. Now that we have seen why this assertion is correct, calculate the boiling point of the aqueous ethylene glycol solution.

Given: composition of solution

Asked for: boiling point

Strategy:

Calculate the molality of ethylene glycol in the 30.2% solution. Then use Equation 11.5.5 to calculate the increase in boiling point.

Solution:

From Example 11.5.1, we know that a 30.2% solution of ethylene glycol in water contains 302 g of ethylene glycol (4.87 mol) per 698 g of water. The molality of the solution is thus

$$\begin{aligned}\text{molality of ethylene glycol} &= \left(\frac{4.87\ mol}{698\ \cancel{g}\ H_2O}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right) \\ &= 6.98\,m\end{aligned}$$

From Equation 11.5.5, the increase in boiling point is therefore

$$\begin{aligned}\Delta T_b &= mK_b \\ &= (6.98\ \cancel{m})(0.51^\circ C/\ \cancel{m}) \\ &= 3.6^\circ C\end{aligned}$$

The boiling point of the solution is thus predicted to be 104°C. With a solute concentration of almost 7 m, however, the assumption of a dilute solution used to obtain Equation 11.5.5 may not be valid.

? Exercise 11.5.3

Assume that a tablespoon (5.00 g) of NaCl is added to 2.00 L of water at 20.0°C, which is then brought to a boil to cook spaghetti. At what temperature will the water boil?

Answer

> 100.04°C, or 100°C to three significant figures. (Recall that 1 mol of NaCl produces 2 mol of dissolved particles. The small increase in temperature means that adding salt to the water used to cook pasta has essentially no effect on the cooking time.)

Freezing Point Depression

The phase diagram in Figure 11.5.4 shows that dissolving a nonvolatile solute in water not only raises the boiling point of the water but also lowers its freezing point. The solid–liquid curve for the solution crosses the line corresponding to $P = 1\,atm$ at a lower temperature than the curve for pure water.

We can understand this result by imagining that we have a sample of water at the normal freezing point temperature, where there is a dynamic equilibrium between solid and liquid. Water molecules are continuously colliding with the ice surface and entering the solid phase at the same rate that water molecules are leaving the surface of the ice and entering the liquid phase. If we dissolve a nonvolatile solute such as glucose in the liquid, the dissolved glucose molecules will reduce the number of collisions per unit time between water molecules and the ice surface because some of the molecules colliding with the ice will be glucose. Glucose, though, has a very different structure than water, and it cannot fit into the ice lattice. Consequently, the presence of glucose molecules in the solution can only decrease the rate at which water molecules in the liquid collide with the ice surface and solidify. Meanwhile, the rate at which the water molecules leave the surface of the ice and enter the liquid phase is unchanged. The net effect is to cause the ice to melt. The only way to reestablish a dynamic equilibrium between solid and liquid water is to lower the temperature of the system, which decreases the rate at which water molecules leave the surface of the ice crystals until it equals the rate at which water molecules in the solution collide with the ice.

By analogy to our treatment of boiling point elevation,the freezing point depression (ΔT_f) is defined as the difference between the freezing point of the pure solvent and the freezing point of the solution:

$$\Delta T_f = T_f^0 - T_f \tag{11.5.6}$$

where T_f^0 is the freezing point of the pure solvent and T_f is the freezing point of the solution.

The order of the terms is reversed compared with Equation 11.5.4 to express the freezing point depression as a positive number. The relationship between ΔT_f and the solute concentration is given by an equation analogous to Equation 11.5.5:

$$\Delta T_f = mK_f \tag{11.5.7}$$

where m is the molality of the solution and K_f is the molal freezing point depression constant for the solvent (in units of °C/m).

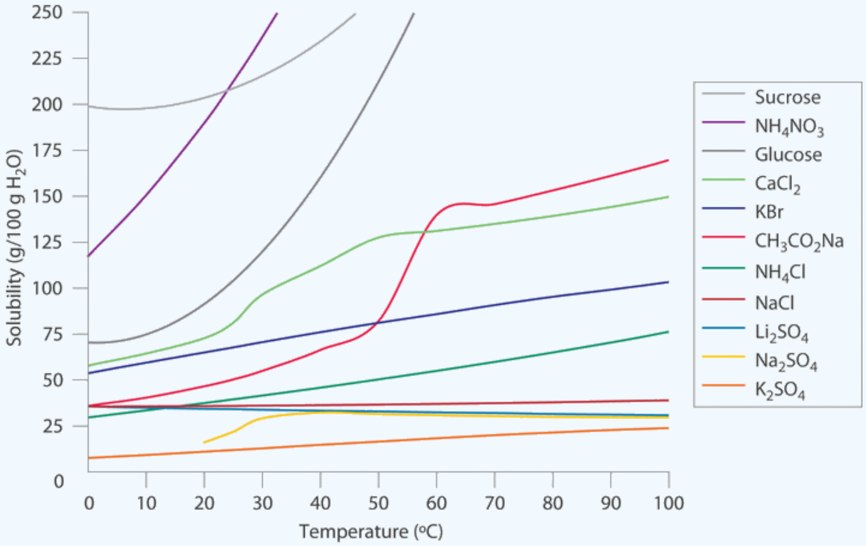
Like K_b, each solvent has a characteristic value of K_f (see Table 11.5.1). Freezing point depression depends on the total number of dissolved nonvolatile solute particles, just as with boiling point elevation. Thus an aqueous NaCl solution has twice as large a freezing point depression as a glucose solution of the same molality.

People who live in cold climates use freezing point depression to their advantage in many ways. For example, salt is used to melt ice and snow on roads and sidewalks, ethylene glycol is added to engine coolant water to prevent an automobile engine from being destroyed, and methanol is added to windshield washer fluid to prevent the fluid from freezing.

> The decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus a pure liquid all depend on the total number of dissolved nonvolatile solute particles.

✓ Example 11.5.4: Salting the Roads

In colder regions of the United States, NaCl or CaCl_2 is often sprinkled on icy roads in winter to melt the ice and make driving safer. Use the data in the Figure below to estimate the concentrations of two saturated solutions at 0°C, one of NaCl and one of CaCl_2, and calculate the freezing points of both solutions to see which salt is likely to be more effective at melting ice.



Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature. Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds. (CC BY-NC-SA; anonymous)

Given: solubilities of two compounds

Asked for: concentrations and freezing points

Strategy:

A. Estimate the solubility of each salt in 100 g of water from the figure. Determine the number of moles of each in 100 g and calculate the molalities.
B. Determine the concentrations of the dissolved salts in the solutions. Substitute these values into Equation 11.5.7 to calculate the freezing point depressions of the solutions.

Solution:

A. From Figure above, we can estimate the solubilities of NaCl and $\mathrm{CaCl_2}$ to be about 36 g and 60 g, respectively, per 100 g of water at 0°C. The corresponding concentrations in molality are

$$m_{NaCl} = \left(\frac{36\ \ g\ \cancel{NaCl}}{100\ \ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ NaCl}{58.44\ \ g\ \cancel{NaCl}}\right)\left(\frac{1000\ \ \cancel{g}}{1\ kg}\right) = 6.2\ m$$

$$m_{CaCl_2} = \left(\frac{60\ \ g\ \cancel{CaCl_2}}{100\ \ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ CaCl_2}{110.98\ \ g\ \cancel{CaCl_2}}\right)\left(\frac{1000\ \ \cancel{g}}{1kg}\right) = 5.4\ m$$

The lower formula mass of NaCl more than compensates for its lower solubility, resulting in a saturated solution that has a slightly higher concentration than $\mathrm{CaCl_2}$.

B. Because these salts are ionic compounds that dissociate in water to yield two and three ions per formula unit of NaCl and $\mathrm{CaCl_2}$, respectively, the actual concentrations of the dissolved species in the two saturated solutions are 2 × 6.2 m = 12 m for NaCl and 3 × 5.4 m = 16 m for $\mathrm{CaCl_2}$. The resulting freezing point depressions can be calculated using Equation 11.5.7:

$$\mathrm{NaCl}: \Delta T_f = mK_f = (12\ \ \cancel{m})(1.86^\circ C/\ \cancel{m}) = 22^\circ C$$

$$\mathrm{CaCl_2}: \Delta T_f = mK_f = (16\ \ \cancel{m})(1.86^\circ C/\ \cancel{m}) = 30^\circ C$$

Because the freezing point of pure water is 0°C, the actual freezing points of the solutions are −22°C and −30°C, respectively. Note that $\mathrm{CaCl_2}$ is substantially more effective at lowering the freezing point of water because its solutions contain three ions per formula unit. In fact, $\mathrm{CaCl_2}$ is the salt usually sold for home use, and it is also often used on highways.

Because the solubilities of both salts decrease with decreasing temperature, the freezing point can be depressed by only a certain amount, regardless of how much salt is spread on an icy road. If the temperature is significantly below the minimum temperature at which one of these salts will cause ice to melt (say −35°C), there is no point in using salt until it gets warmer

? Exercise 11.5.4

Calculate the freezing point of the 30.2% solution of ethylene glycol in water whose vapor pressure and boiling point we calculated in Examples 11.5.1 and 11.5.3.

Answer

−13.0°C

✓ Example 11.5.5

Arrange these aqueous solutions in order of decreasing freezing points: 0.1 m KCl, 0.1 m glucose, 0.1 m $\mathrm{SrCl_2}$, 0.1 m ethylene glycol, 0.1 m benzoic acid, and 0.1 m HCl.

Given: molalities of six solutions

Asked for: relative freezing points

Strategy:

A. Identify each solute as a strong, weak, or nonelectrolyte, and use this information to determine the number of solute particles produced.

B. Multiply this number by the concentration of the solution to obtain the effective concentration of solute particles. The solution with the highest effective concentration of solute particles has the largest freezing point depression.

Solution:

A Because the molal concentrations of all six solutions are the same, we must focus on which of the substances are strong electrolytes, which are weak electrolytes, and which are nonelectrolytes to determine the actual numbers of particles in solution. KCl, $\mathrm{SrCl_2}$, and HCl are **strong electrolytes**, producing two, three, and two ions per formula unit, respectively. Benzoic acid is a weak electrolyte (approximately one particle per molecule), and glucose and ethylene glycol are both nonelectrolytes (one particle per molecule).

B The molalities of the solutions in terms of the total particles of solute are: KCl and HCl, 0.2 m; $SrCl_2$, 0.3 m; glucose and ethylene glycol, 0.1 m; and benzoic acid, 0.1–0.2 m. Because the magnitude of the decrease in freezing point is proportional to the concentration of dissolved particles, the order of freezing points of the solutions is: glucose and ethylene glycol (highest freezing point, smallest freezing point depression) > benzoic acid > HCl = KCl > $\mathrm{SrCl_2}$.

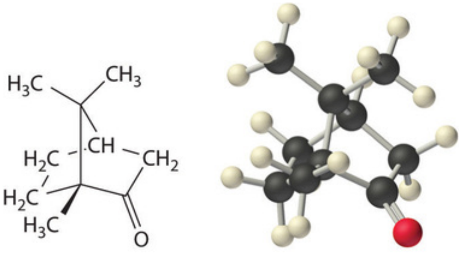
? Exercise 11.5.5

Arrange these aqueous solutions in order of increasing freezing points: 0.2 m NaCl, 0.3 m acetic acid, 0.1 m $\mathrm{CaCl_2}$, and 0.2 m sucrose.

Answer

0.2 m NaCl (lowest freezing point) < 0.3 m acetic acid ≈ 0.1 m $\mathrm{CaCl_2}$ < 0.2 m sucrose (highest freezing point)

Colligative properties can also be used to determine the molar mass of an unknown compound. One method that can be carried out in the laboratory with minimal equipment is to measure the freezing point of a solution with a known mass of solute. This method is accurate for dilute solutions (≤1% by mass) because changes in the freezing point are usually large enough to measure accurately and precisely. By comparing K_b and K_f values in Table $11.5.1$, we see that changes in the boiling point are smaller than changes in the freezing point for a given solvent. Boiling point elevations are thus more difficult to measure precisely. For this reason, freezing point depression is more commonly used to determine molar mass than is boiling point elevation. Because of its very large value of K_f (37.8°C/m), d-(+)-camphor (Table $11.5.1$) is often used to determine the molar mass of organic compounds by this method.



d-(+)-Camphor

✓ Example 11.5.6: Sulfur

A 7.08 g sample of elemental sulfur is dissolved in 75.0 g of CS_2 to create a solution whose freezing point is −113.5°C. Use these data to calculate the molar mass of elemental sulfur and thus the formula of the dissolved Sn molecules (i.e., what is the value of n?).

Given: masses of solute and solvent and freezing point

Asked for: molar mass and number of S atoms per molecule

Strategy:

A. Use Equation 11.5.6, the measured freezing point of the solution, and the freezing point of CS_2 from Table $11.5.1$ to calculate the freezing point depression. Then use Equation 11.5.7 and the value of K_f from Table $11.5.1$ to calculate the molality of the solution.

B. From the calculated molality, determine the number of moles of solute present.
C. Use the mass and number of moles of the solute to calculate the molar mass of sulfur in solution. Divide the result by the molar mass of atomic sulfur to obtain n, the number of sulfur atoms per mole of dissolved sulfur.

Solution:

A The first step is to calculate the freezing point depression using Equation 11.5.6:

$$\Delta T_f = T_f^0 - T_f = -112.1^\circ C - (-113.5^\circ C) = 1.4^\circ C$$

Then Equation 11.5.7 gives

$$m = \frac{\Delta T_f}{K_f} = \frac{1.4^\circ\ \cancel{C}}{3.74^\circ\ \cancel{C}/m} = 0.37\ m$$

B The total number of moles of solute present in the solution is

$$\text{moles solute} = \left(\frac{0.37 mol}{\cancel{kg}}\right)(75.0\ g)\left(\frac{1 kg}{1000\ g}\right) = 0.028\ mol$$

C We now know that 0.708 g of elemental sulfur corresponds to 0.028 mol of solute. The molar mass of dissolved sulfur is thus

$$\text{molar mass} = \frac{7.08\ g}{0.028\ mol} = 260\ g/mol$$

The molar mass of atomic sulfur is 32 g/mol, so there must be 260/32 = 8.1 sulfur atoms per mole, corresponding to a formula of S_8.

? Exercise 11.5.6

One of the byproducts formed during the synthesis of C_{60} is a deep red solid containing only carbon. A solution of 205 mg of this compound in 10.0 g of CCl_4 has a freezing point of −23.38°C. What are the molar mass and most probable formula of the substance?

Answer

847 g/mol; C_{70}

Osmotic Pressure

Osmotic pressure is a colligative property of solutions that is observed using a semipermeable membrane, a barrier with pores small enough to allow solvent molecules to pass through but not solute molecules or ions. The net flow of solvent through a semipermeable membrane is called osmosis (from the Greek osmós, meaning "push"). The direction of net solvent flow is always from the side with the lower concentration of solute to the side with the higher concentration.

Osmosis can be demonstrated using a U-tube like the one shown in Figure 11.5.6, which contains pure water in the left arm and a dilute aqueous solution of glucose in the right arm. A net flow of water through the membrane occurs until the levels in the arms eventually stop changing, which indicates that equilibrium has been reached. The osmotic pressure (Π) of the glucose solution is the difference in the pressure between the two sides, in this case the heights of the two columns. Although the semipermeable membrane allows water molecules to flow through in either direction, the rate of flow is not the same in both directions because the concentration of water is not the same in the two arms. The net flow of water through the membrane can be prevented by applying a pressure to the right arm that is equal to the osmotic pressure of the glucose solution.

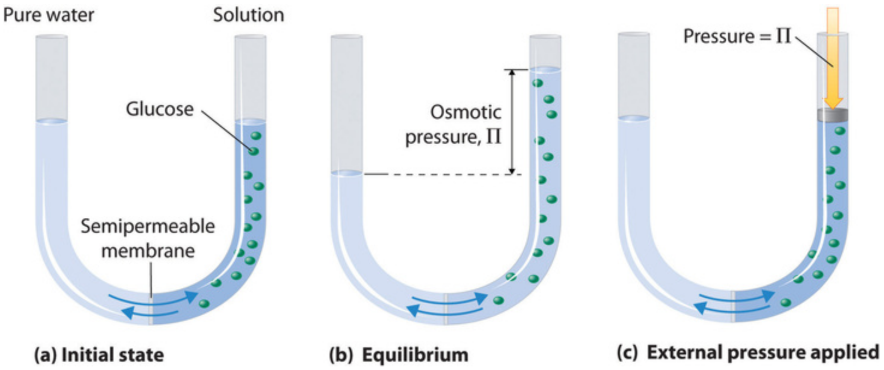


Figure 11.5.6: Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution (Π_{soln}), equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation. (CC BY-NC-SA; anonymous)

Just as with any other colligative property, the osmotic pressure of a solution depends on the concentration of dissolved solute particles. Osmotic pressure obeys a law that resembles the ideal gas equation:

$$\Pi = \frac{nRT}{V} = MRT \tag{11.5.8}$$

where M is the number of moles of solute per unit volume of solution (i.e., the molarity of the solution), R is the ideal gas constant, and T is the absolute temperature.

As shown in Example $11.5.7$, osmotic pressures tend to be quite high, even for rather dilute solutions.

✓ Example $11.5.7$

When placed in a concentrated salt solution, certain yeasts are able to produce high internal concentrations of glycerol to counteract the osmotic pressure of the surrounding medium. Suppose that the yeast cells are placed in an aqueous solution containing 4.0% NaCl by mass; the solution density is 1.02 g/mL at 25°C.

a. Calculate the osmotic pressure of a 4.0% aqueous NaCl solution at 25°C.
b. If the normal osmotic pressure inside a yeast cell is 7.3 atm, corresponding to a total concentration of dissolved particles of 0.30 M, what concentration of glycerol must the cells synthesize to exactly balance the external osmotic pressure at 25°C?

Given: concentration, density, and temperature of NaCl solution; internal osmotic pressure of cell

Asked for: osmotic pressure of NaCl solution and concentration of glycerol needed

Strategy:

A. Calculate the molarity of the NaCl solution using the formula mass of the solute and the density of the solution. Then calculate the total concentration of dissolved particles.
B. Use Equation $11.5.8$ to calculate the osmotic pressure of the solution.
C. Subtract the normal osmotic pressure of the cells from the osmotic pressure of the salt solution to obtain the additional pressure needed to balance the two. Use Equation $11.5.8$ to calculate the molarity of glycerol needed to create this osmotic pressure.

Solution:

A The solution contains 4.0 g of NaCl per 100 g of solution. Using the formula mass of NaCl (58.44 g/mol) and the density of the solution (1.02 g/mL), we can calculate the molarity:

$$\begin{aligned} M_{NaCl} &= \frac{moles\ NaCl}{\text{liter solution}} \\ &= \left(\frac{4.0\ \cancel{g}\ NaCl}{58.44\ \cancel{g}/mol\ NaCl}\right)\left(\frac{1}{100\ \ g\ \cancel{solution}}\right)\left(\frac{1.02\ \ g\ \cancel{solution}}{1.00\ \ m\cancel{L}\ solution}\right)\left(\frac{1000\ \ m\cancel{L}}{1\ L}\right) \\ &= 0.70\ M\ \text{NaCl} \end{aligned}$$

Because 1 mol of NaCl produces 2 mol of particles in solution, the total concentration of dissolved particles in the solution is (2)(0.70 M) = 1.4 M.

B Now we can use Equation 11.5.8 to calculate the osmotic pressure of the solution:

$$\begin{aligned} \Pi &= MRT \\ &= (1.4\ mol/L)\left[0.0821\ (L \cdot atm)/(K \cdot mol)\right](298\ K) \\ &= 34\ atm \end{aligned}$$

C If the yeast cells are to exactly balance the external osmotic pressure, they must produce enough glycerol to give an additional internal pressure of (34 atm − 7.3 atm) = 27 atm. Glycerol is a nonelectrolyte, so we can solve Equation 11.5.8 for the molarity corresponding to this osmotic pressure:

$$\begin{aligned} M &= \frac{\Pi}{RT} \\ &= \frac{27\ \ \cancel{atm}}{[0.0821(L \cdot\ \cancel{atm})/(\ \cancel{K} \cdot mol)](298\ \ \cancel{K})} \\ &= 1.1\ M\ \text{glycerol} \end{aligned}$$

In solving this problem, we could also have recognized that the only way the osmotic pressures can be the same inside the cells and in the solution is if the concentrations of dissolved particles are the same. We are given that the normal concentration of dissolved particles in the cells is 0.3 M, and we have calculated that the NaCl solution is effectively 1.4 M in dissolved particles. The yeast cells must therefore synthesize enough glycerol to increase the internal concentration of dissolved particles from 0.3 M to 1.4 M—that is, an additional 1.1 M concentration of glycerol.

? Exercise 11.5.7

Assume that the fluids inside a sausage are approximately 0.80 M in dissolved particles due to the salt and sodium nitrite used to prepare them. Calculate the osmotic pressure inside the sausage at 100°C to learn why experienced cooks pierce the semipermeable skin of sausages before boiling them.

Answer

24 atm

Because of the large magnitude of osmotic pressures, osmosis is extraordinarily important in biochemistry, biology, and medicine. Virtually every barrier that separates an organism or cell from its environment acts like a semipermeable membrane, permitting the flow of water but not solutes. The same is true of the compartments inside an organism or cell. Some specialized barriers, such as those in your kidneys, are slightly more permeable and use a related process called dialysis, which permits both water and small molecules to pass through but not large molecules such as proteins.

The same principle has long been used to preserve fruits and their essential vitamins over the long winter. High concentrations of sugar are used in jams and jellies not for sweetness alone but because they greatly increase the osmotic pressure. Thus any bacteria not killed in the cooking process are dehydrated, which keeps them from multiplying in an otherwise rich medium for bacterial growth. A similar process using salt prevents bacteria from growing in ham, bacon, salt pork, salt cod, and other preserved meats. The effect of osmotic pressure is dramatically illustrated in Figure 11.5.7, which shows what happens when red blood cells are placed in a solution whose osmotic pressure is much lower or much higher than the internal pressure of the cells.

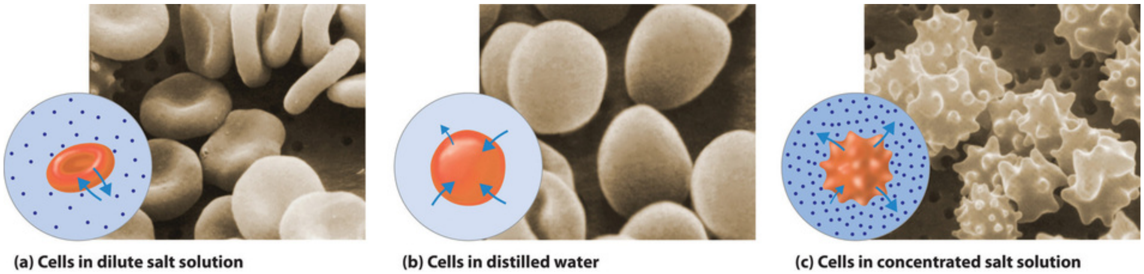


Figure 11.5.7: Effect on Red Blood Cells of the Surrounding Solution's Osmotic Pressure. (a) When red blood cells are placed in a dilute salt solution having the same osmotic pressure as the intracellular fluid, the rate of flow of water into and out of the cells is the same and their shape does not change. (b) When cells are placed in distilled water whose osmotic pressure is less than that of the intracellular fluid, the rate of flow of water into the cells is greater than the rate of flow out of the cells. The cells swell and eventually burst. (c) When cells are placed in a concentrated salt solution with an osmotic pressure greater than that of the intracellular fluid, the rate of flow of water out of the cells is greater than the rate of flow into the cells. The cells shrivel and become so deformed that they cannot function. (CC BY-NC-SA; anonymous)

In addition to capillary action, trees use osmotic pressure to transport water and other nutrients from the roots to the upper branches. Evaporation of water from the leaves results in a local increase in the salt concentration, which generates an osmotic pressure that pulls water up the trunk of the tree to the leaves.

Finally, a process called reverse osmosis can be used to produce pure water from seawater. As shown schematically in Figure 11.5.8, applying high pressure to seawater forces water molecules to flow through a semipermeable membrane that separates pure water from the solution, leaving the dissolved salt behind. Large-scale desalinization plants that can produce hundreds of thousands of gallons of freshwater per day are common in the desert lands of the Middle East, where they supply a large proportion of the freshwater needed by the population. Similar facilities are now being used to supply freshwater in southern California. Small, hand-operated reverse osmosis units can produce approximately 5 L of freshwater per hour, enough to keep 25 people alive, and are now standard equipment on US Navy lifeboats.

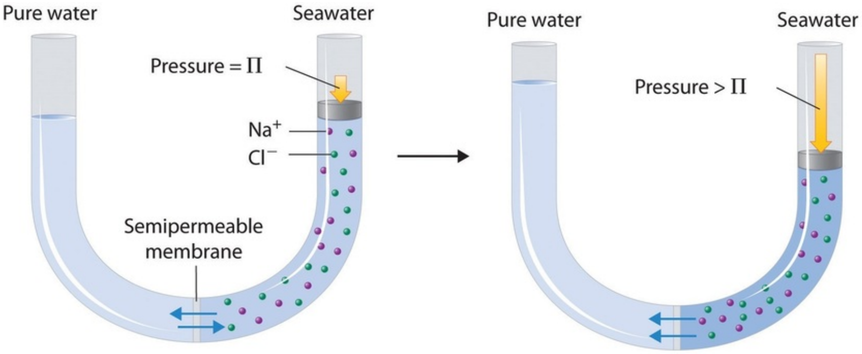


Figure 11.5.8: Desalinization of Seawater by Reverse Osmosis. (top) When the pressure applied to seawater equals its osmotic pressure (Π_{soln}), there is no net flow of water across the semipermeable membrane. (bottom) The application of pressure greater than the osmotic pressure of seawater forces water molecules to flow through the membrane, leaving behind a concentrated salt solution. In desalinization plants, seawater is continuously introduced under pressure and pure water is collected, so the process continues indefinitely. (CC BY-NC-SA; anonymous)

Colligative Properties of Electrolyte Solutions

Thus far we have assumed that we could simply multiply the molar concentration of a solute by the number of ions per formula unit to obtain the actual concentration of dissolved particles in an electrolyte solution. We have used this simple model to predict such properties as freezing points, melting points, vapor pressure, and osmotic pressure. If this model were perfectly correct, we would expect the freezing point depression of a 0.10 m solution of sodium chloride, with 2 mol of ions per mole of $NaCl$ in solution, to be exactly twice that of a 0.10 m solution of glucose, with only 1 mol of molecules per mole of glucose in solution. In reality, this is not always the case. Instead, the observed change in freezing points for 0.10 m aqueous solutions of $NaCl$ and KCl are significantly less than expected (−0.348°C and −0.344°C, respectively, rather than −0.372°C), which suggests that fewer particles than we expected are present in solution.

The relationship between the actual number of moles of solute added to form a solution and the apparent number as determined by colligative properties is called the van 't Hoff factor (i) and is defined as follows:

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}} \tag{11.5.9}$$

Named for Jacobus Hendricus van ’t Hoff (1852–1911), a Dutch chemistry professor at the University of Amsterdam who won the first Nobel Prize in Chemistry (1901) for his work on thermodynamics and solutions.

> *As the solute concentration increases, the van ’t Hoff factor decreases.*

The van ’t Hoff factor is therefore **a measure of a deviation from ideal behavior**. The lower the van ’t Hoff factor, the greater the deviation. As the data in Table $11.5.2$ show, the van ’t Hoff factors for ionic compounds are somewhat lower than expected; that is, their solutions apparently contain fewer particles than predicted by the number of ions per formula unit. As the concentration of the solute increases, the van ’t Hoff factor decreases because ionic compounds generally do not totally dissociate in aqueous solution.

Table 11.5.2: van ’t Hoff Factors for 0.0500 M Aqueous Solutions of Selected Compounds at 25°C

Compound	i (measured)	i (ideal)
glucose	1.0	1.0
sucrose	1.0	1.0
$NaCl$	1.9	2.0
HCl	1.9	2.0
$MgCl_2$	2.7	3.0
$FeCl_3$	3.4	4.0
$Ca(NO_3)_2$	2.5	3.0
$AlCl_3$	3.2	4.0
$MgSO_4$	1.4	2.0

Instead, some of the ions exist as ion pairs, a cation and an anion that for a brief time are associated with each other without an intervening shell of water molecules (Figure $11.5.9$). Each of these temporary units behaves like a single dissolved particle until it dissociates. Highly charged ions such as Mg^{2+}, Al^{3+}, SO_4^{2-}, and PO_4^{3-} have a greater tendency to form ion pairs because of their strong electrostatic interactions. The actual number of solvated ions present in a solution can be determined by measuring a colligative property at several solute concentrations.

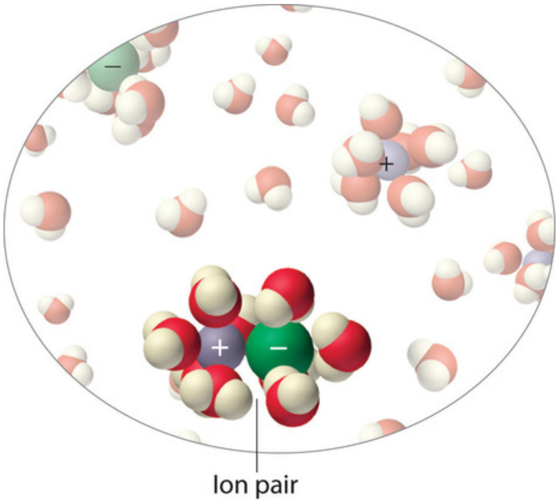


Figure 11.5.9: Ion Pairs. In concentrated solutions of electrolytes like $NaCl$, some of the ions form neutral ion pairs that are not separated by solvent and diffuse as single particles.

✓ Example 11.5.8: Iron Chloride in Water

A 0.0500 M aqueous solution of $FeCl_3$ has an osmotic pressure of 4.15 atm at 25°C. Calculate the van ’t Hoff factor i for the solution.

Given: solute concentration, osmotic pressure, and temperature

Asked for: van ’t Hoff factor

Strategy:

A. Use Equation 11.5.8 to calculate the expected osmotic pressure of the solution based on the effective concentration of dissolved particles in the solvent.
B. Calculate the ratio of the observed osmotic pressure to the expected value. Multiply this number by the number of ions of solute per formula unit, and then use Equation 11.5.9 to calculate the van ’t Hoff factor.

Solution:

A If $FeCl_3$ dissociated completely in aqueous solution, it would produce four ions per formula unit (one $Fe^{3+}(aq)$ and three \(\ce{Cl^{-}(aq)} ions) for an effective concentration of dissolved particles of 4 × 0.0500 M = 0.200 M. The osmotic pressure would be

$$\begin{aligned}\Pi &= MRT \\ &= (0.200\ mol/L)\,[0.0821\ (L\cdot atm)/(K\cdot mol)]\,(298\ K) = 4.89\ atm\end{aligned}$$

B The observed osmotic pressure is only 4.15 atm, presumably due to ion pair formation. The ratio of the observed osmotic pressure to the calculated value is 4.15 atm/4.89 atm = 0.849, which indicates that the solution contains (0.849)(4) = 3.40 moles of particles per mole of $FeCl_3$ dissolved. Alternatively, we can calculate the observed particle concentration from the osmotic pressure of 4.15 atm:

$$4.15\ atm = M\left(\frac{0.0821\ (L\cdot atm)}{(K\cdot mol)}\right)(298\ K)$$

or after rearranging

$$M = 0.170 mol$$

The ratio of this value to the expected value of 0.200 M is 0.170 M/0.200 M = 0.850, which again gives us (0.850)(4) = 3.40 mole of particles per mole of $FeCl_3$ dissolved. From Equation 11.5.9, the van ’t Hoff factor for the solution is

$$i = \frac{3.40 \text{ particles observed}}{1 \text{ formula unit } FeCl_3} = 3.40$$

? Exercise 11.5.8: Magnesium Chloride in Water

Calculate the van ’t Hoff factor for a 0.050 m aqueous solution of $MgCl_2$ that has a measured freezing point of −0.25°C.

Answer

2.7 (versus an ideal value of 3).

Summary

The colligative properties of a solution depend on only the total number of dissolved particles in solution, not on their chemical identity. Colligative properties include vapor pressure, boiling point, freezing point, and osmotic pressure. The addition of a nonvolatile solute (one without a measurable vapor pressure) decreases the vapor pressure of the solvent. The vapor pressure of the solution is proportional to the mole fraction of solvent in the solution, a relationship known as **Raoult’s law**. The boiling point elevation (ΔT_b) and freezing point depression (ΔT_f) of a solution are defined as the differences between the boiling and freezing points, respectively, of the solution and the pure solvent. Both are proportional to the molality of the solute. When a solution and a pure solvent are separated by a semipermeable membrane, a barrier that allows solvent molecules but not solute molecules to pass through, the flow of solvent in opposing directions is unequal and produces an osmotic pressure, which is the difference in pressure between the two sides of the membrane. Osmosis is the net flow of solvent through such a membrane due to different solute concentrations. Dialysis uses a semipermeable membrane with pores that allow only small solute molecules and solvent molecules to pass through. In more concentrated solutions, or in solutions of salts with highly charged ions, the cations and anions can associate to form ion pairs, which decreases their effect on the colligative properties of the solution. The extent of ion pair formation is given by the van ’t Hoff factor (i), the ratio of the apparent number of particles in solution to the number predicted by the stoichiometry of the salt.

- **Henry’s law:**

$$C = kP$$

- **Raoult’s law**:

$$P_A = \chi_A P^0_A$$

- **vapor pressure lowering**:

$$P^0_A - P_A = \Delta P_A = \chi_B P^0_A$$

- **vapor pressure of a system containing two volatile components**:

$$P_{tot} = \chi_A P^0_A + (1 - \chi_A) P^0_B$$

- **boiling point elevation**:

$$\Delta T_b = m K_b$$

- **freezing point depression:**

$$\Delta T_f = m K_f$$

- **osmotic pressure**:

$$\Pi = \frac{n}{V} RT = MRT$$

- **van ’t Hoff factor**:

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}}$$

11.6: Phase Equilibrium in Solutions - Volatile Solutes

Learning Objectives

- To understand the relationship among temperature, pressure, and solubility.
- The understand that the solubility of a solid may increase or decrease with increasing temperature,
- To understand that the solubility of a gas decreases with an increase in temperature and a decrease in pressure.

Effect of Pressure on the Solubility of Gases: Henry's Law

External pressure has very little effect on the solubility of liquids and solids. In contrast, the solubility of gases increases as the partial pressure of the gas above a solution increases. This point is illustrated in Figure 11.6.1, which shows the effect of increased pressure on the dynamic equilibrium that is established between the dissolved gas molecules in solution and the molecules in the gas phase above the solution. Because the concentration of molecules in the gas phase increases with increasing pressure, the concentration of dissolved gas molecules in the solution at equilibrium is also higher at higher pressures.

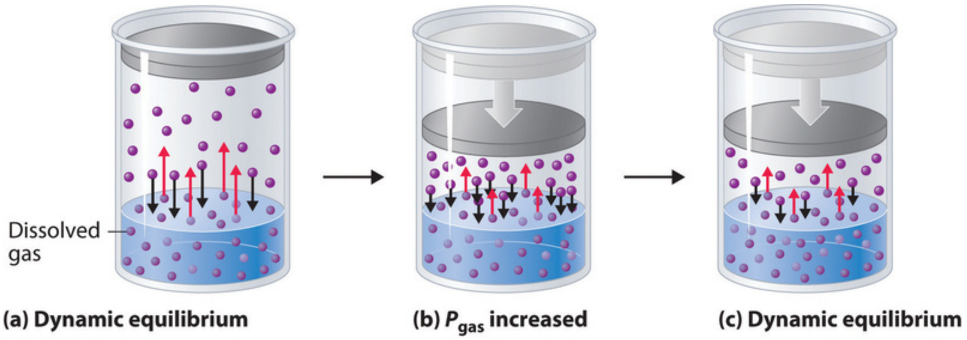


Figure 11.6.1: A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature. (a) When a gas comes in contact with a pure liquid, some of the gas molecules (purple spheres) collide with the surface of the liquid and dissolve. When the concentration of dissolved gas molecules has increased so that the rate at which gas molecules escape into the gas phase is the same as the rate at which they dissolve, a dynamic equilibrium has been established, as depicted here. This equilibrium is entirely analogous to the one that maintains the vapor pressure of a liquid. (b) Increasing the pressure of the gas increases the number of molecules of gas per unit volume, which increases the rate at which gas molecules collide with the surface of the liquid and dissolve. (c) As additional gas molecules dissolve at the higher pressure, the concentration of dissolved gas increases until a new dynamic equilibrium is established.

The relationship between pressure and the solubility of a gas is described quantitatively by Henry's law, which is named for its discoverer, the English physician and chemist, William Henry (1775–1836):

$$C = k_H P \tag{11.6.1}$$

where C is the concentration of dissolved gas at equilibrium, P is the partial pressure of the gas, and k_H is the Henry's law constant, which must be determined experimentally for each combination of gas, solvent, and temperature.

Although the gas concentration may be expressed in any convenient units, we will use molarity exclusively. The units of the Henry's law constant are therefore mol/(L·atm) = M/atm. Values of the Henry's law constants for solutions of several gases in water at 20°C are listed in Table 11.6.1.

As the data in Table 11.6.1 demonstrate, the concentration of a dissolved gas in water at a given pressure depends strongly on its physical properties. For a series of related substances, London dispersion forces increase as molecular mass increases. Thus among the elements of Group 18, the Henry's law constants increase smoothly from He to Ne to Ar. The table also shows that O_2 is almost twice as soluble as N_2. Although London dispersion forces are too weak to explain such a large difference, O_2 is paramagnetic and hence more polarizable than N_2, which explains its high solubility.

Table 11.6.1: Henry's Law Constants for Selected Gases in Water at 20°C

Gas	Henry's Law Constant [mol/(L·atm)] × 10^{-4}
Ar	15
CO_2	392

Gas	Henry's Law Constant [mol/(L·atm)] × 10^{-4}
H_2	8.1
He	3.9
N_2	7.1
Ne	4.7
O_2	14

Gases that react with the solvent do not obey Henry's law

Gases that react chemically with water, such as HCl and the other hydrogen halides, $\mathrm{H_2S}$, and $\mathrm{NH_3}$, do not obey Henry's law; all of these gases are much more soluble than predicted by Henry's law. For example, HCl reacts with water to give $\mathrm{H^+(aq)}$ and $\mathrm{Cl^-(aq)}$, not dissolved HCl molecules,

$$\mathrm{HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)}$$

The dissociation of HCl into ions results in a much higher effective "solubility" than expected for a neutral molecule.

Jan 3, 2019, 5:36 PM

https://en.Wikipedia.org/wiki/Henry%...constants_Heff

https://www.sciencedirect.com/scienc...0469818690079X

https://www.atmos-chem-phys.net/15/4...-4399-2015.pdf

Henry's law has important applications. For example, bubbles of $\mathrm{CO_2}$ form as soon as a carbonated beverage is opened because the drink was bottled under $\mathrm{CO_2}$ at a pressure greater than 1 atm. When the bottle is opened, the pressure of $\mathrm{CO_2}$ above the solution drops rapidly, and some of the dissolved gas escapes from the solution as bubbles. Henry's law also explains why scuba divers have to be careful to ascend to the surface slowly after a dive if they are breathing compressed air. At the higher pressures under water, more $\mathrm{N_2}$ from the air dissolves in the diver's internal fluids. If the diver ascends too quickly, the rapid pressure change causes small bubbles of $\mathrm{N_2}$ to form throughout the body, a condition known as "the bends." These bubbles can block the flow of blood through the small blood vessels, causing great pain and even proving fatal in some cases.

Due to the low Henry's law constant for $\mathrm{O_2}$ in water, the levels of dissolved oxygen in water are too low to support the energy needs of multicellular organisms, including humans. To increase the $\mathrm{O_2}$ concentration in internal fluids, organisms synthesize highly soluble carrier molecules that bind $\mathrm{O_2}$ reversibly. For example, human red blood cells contain a protein called hemoglobin that specifically binds $\mathrm{O_2}$ and facilitates its transport from the lungs to the tissues, where it is used to oxidize food molecules to provide energy. The concentration of hemoglobin in normal blood is about 2.2 mM, and each hemoglobin molecule can bind four $\mathrm{O_2}$ molecules. Although the concentration of dissolved $\mathrm{O_2}$ in blood serum at 37°C (normal body temperature) is only 0.010 mM, the total dissolved $\mathrm{O_2}$ concentration is 8.8 mM, almost a thousand times greater than would be possible without hemoglobin. Synthetic oxygen carriers based on fluorinated alkanes have been developed for use as an emergency replacement for whole blood. Unlike donated blood, these "blood substitutes" do not require refrigeration and have a long shelf life. Their very high Henry's law constants for $\mathrm{O_2}$ result in dissolved oxygen concentrations comparable to those in normal blood.

Example 11.6.1: Oxygen in Water

The Henry's law constant for $\mathrm{O_2}$ in water at 25°C is $1.27 \times 10^{-3}\, M/atm$, and the mole fraction of $\mathrm{O_2}$ in the atmosphere is 0.21. Calculate the solubility of $\mathrm{O_2}$ in water at 25°C at an atmospheric pressure of 1.00 atm.

Given: Henry's law constant, mole fraction of $\mathrm{O_2}$, and pressure

Asked for: solubility

Strategy:

A. Use Dalton's law of partial pressures to calculate the partial pressure of oxygen.
B. Use Henry's law (Equation 11.6.1) to calculate the solubility, expressed as the concentration of dissolved gas.

Solution:

A According to Dalton’s law, the partial pressure of O_2 is proportional to the mole fraction of O_2:

$$P_A = \chi_A P_t = (0.21)(1.00\ atm) = 0.21\ atm$$

B From Henry’s law, the concentration of dissolved oxygen under these conditions is

$$CO_2 = k_H P_{O_2} = (1.27 \times 10^{-3}\ M/\ \cancel{atm})(0.21\ \ \cancel{atm}) = 2.7 \times 10^{-4}\ M$$

? Exercise 11.6.1: Carbon Dioxide in Water

To understand why soft drinks “fizz” and then go “flat” after being opened, calculate the concentration of dissolved CO_2 in a soft drink:

a. bottled under a pressure of 5.0 atm of CO_2
b. in equilibrium with the normal partial pressure of CO_2 in the atmosphere (approximately $3 \times 10^{-4}\ atm$). The Henry’s law constant for CO_2 in water at 25°C is $3.4 \times 10^{-2}\ M/atm$.

Answer a

0.17 M

Answer b

$1 \times 10^{-5} M$

Summary

The solubility of most substances depends strongly on the temperature and, in the case of gases, on the pressure. The solubility of most solid or liquid solutes increases with increasing temperature. The components of a mixture can often be separated using fractional crystallization, which separates compounds according to their solubilities. The solubility of a gas decreases with increasing temperature. Henry’s law describes the relationship between the pressure and the solubility of a gas.

11.7: Colloidal Suspensions

Learning Objectives

- To distinguish between true solutions and solutions with aggregate particles.

Suspensions and colloids are two common types of mixtures whose properties are in many ways intermediate between those of true solutions and heterogeneous mixtures. A suspension is a heterogeneous mixture of particles with diameters of about 1 µm (1000 nm) that are distributed throughout a second phase. Common suspensions include paint, blood, and hot chocolate, which are solid particles in a liquid, and aerosol sprays, which are liquid particles in a gas. If the suspension is allowed to stand, the two phases will separate, which is why paints must be thoroughly stirred or shaken before use. A colloid is also a heterogeneous mixture, but the particles of a colloid are typically smaller than those of a suspension, generally in the range of 2 to about 500 nm in diameter. Colloids include fog and clouds (liquid particles in a gas), milk (solid particles in a liquid), and butter (solid particles in a solid). Other colloids are used industrially as catalysts. Unlike in a suspension, the particles in a colloid do not separate into two phases on standing. The only combination of substances that cannot produce a suspension or a colloid is a mixture of two gases because their particles are so small that they always form true solutions. The properties of suspensions, colloids, and solutions are summarized in Table $11.7.1$.

Table $11.7.1$: Properties of Liquid Solutions, Colloids, and Suspensions

Type of Mixture	Approximate Size of Particles (nm)	Characteristic Properties	Examples
solution	< 2	not filterable; does not separate on standing; does not scatter visible light	air, white wine, gasoline, salt water
colloid	2–500	scatters visible light; translucent or opaque; not filterable; does not separate on standing	smoke, fog, ink, milk, butter, cheese
suspension	500–1000	cloudy or opaque; filterable; separates on standing	muddy water, hot cocoa, blood, paint

Colloids and Suspensions

Colloids were first characterized in about 1860 by Thomas Graham, who also gave us Graham’s law of diffusion and effusion. Although some substances, such as starch, gelatin, and glue, appear to dissolve in water to produce solutions, Graham found that they diffuse very slowly or not at all compared with solutions of substances such as salt and sugar. Graham coined the word colloid (from the Greek kólla, meaning “glue”) to describe these substances, as well as the words sol and gel to describe certain types of colloids in which all of the solvent has been absorbed by the solid particles, thus preventing the mixture from flowing readily, as we see in Jell-O. Two other important types of colloids are aerosols, which are dispersions of solid or liquid particles in a gas, and emulsions, which are dispersions of one liquid in another liquid with which it is immiscible.

Colloids share many properties with solutions. For example, the particles in both are invisible without a powerful microscope, do not settle on standing, and pass through most filters. However, the particles in a colloid scatter a beam of visible light, a phenomenon known as the Tyndall effect,The effect is named after its discoverer, John Tyndall, an English physicist (1820–1893). whereas the particles of a solution do not. The Tyndall effect is responsible for the way the beams from automobile headlights are clearly visible from the side on a foggy night but cannot be seen from the side on a clear night. It is also responsible for the colored rays of light seen in many sunsets, where the sun’s light is scattered by water droplets and dust particles high in the atmosphere. An example of the Tyndall effect is shown in Figure $11.7.1$.

Figure 11.7.1: Tyndall Effect, the Scattering of Light by Colloids (CC BY; LibreTexts)

Although colloids and suspensions can have particles similar in size, the two differ in stability: the particles of a colloid remain dispersed indefinitely unless the temperature or chemical composition of the dispersing medium is changed. The chemical explanation for the stability of colloids depends on whether the colloidal particles are hydrophilic or hydrophobic.

Most proteins, including those responsible for the properties of gelatin and glue, are hydrophilic because their exterior surface is largely covered with polar or charged groups. Starch, a long-branched polymer of glucose molecules, is also hydrophilic. A hydrophilic colloid particle interacts strongly with water, resulting in a shell of tightly bound water molecules that prevents the particles from aggregating when they collide. Heating such a colloid can cause aggregation because the particles collide with greater energy and disrupt the protective shell of solvent. Moreover, heat causes protein structures to unfold, exposing previously buried hydrophobic groups that can now interact with other hydrophobic groups and cause the particles to aggregate and precipitate from solution. When an egg is boiled, for example, the egg white, which is primarily a colloidal suspension of a protein called albumin, unfolds and exposes its hydrophobic groups, which aggregate and cause the albumin to precipitate as a white solid.

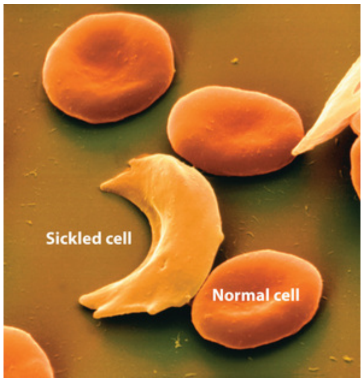


Figure 11.7.2: Sickle-Cell Anemia The characteristic shape of sickled red blood cells is the result of fibrous aggregation of hemoglobin molecules inside the cell.

A normal blood cell is circular in shape with a dimple in the middle, a sickled cell is banana shaped.

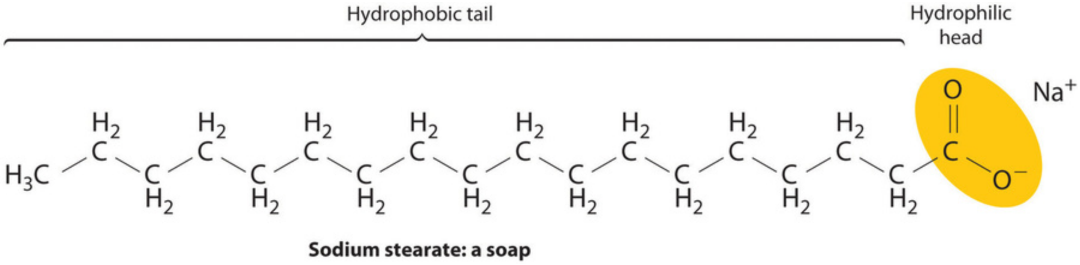
In some cases, a stable colloid can be transformed to an aggregated suspension by a minor chemical modification. Consider, for example, the behavior of hemoglobin, a major component of red blood cells. Hemoglobin molecules normally form a colloidal suspension inside red blood cells, which typically have a “donut” shape and are easily deformed, allowing them to squeeze through the capillaries to deliver oxygen to tissues. In a common inherited disease called sickle-cell anemia, one of the amino acids in hemoglobin that has a hydrophilic carboxylic acid side chain (glutamate) is replaced by another amino acid that has a hydrophobic side chain (valine). Under some conditions, the abnormal hemoglobin molecules can aggregate to form long, rigid fibers that cause the red blood cells to deform, adopting a characteristic sickle shape that prevents them from passing through the capillaries (Figure 11.7.2). The reduction in blood flow results in severe cramps, swollen joints, and liver damage. Until recently, many patients with sickle-cell anemia died before the age of 30 from infection, blood clots, or heart or kidney failure, although individuals with the sickle-cell genetic trait are more resistant to malaria than are those with “normal” hemoglobin.

Figure 11.7.3: Formation of New Land by the Destabilization of a Colloid Suspension. This satellite photograph shows the Mississippi River delta from New Orleans (top) to the Gulf of Mexico (bottom). Where seawater mixes with freshwater from the Mississippi River, colloidal clay particles in the river water precipitate (tan area).

Aggregation and precipitation can also result when the outer, charged layer of a particle is neutralized by ions with the opposite charge. In inland waterways, clay particles, which have a charged surface, form a colloidal suspension. High salt concentrations in seawater neutralize the charge on the particles, causing them to precipitate and form land at the mouths of large rivers, as seen in the satellite view in Figure 11.7.3. Charge neutralization is also an important strategy for precipitating solid particles from gaseous colloids such as smoke, and it is widely used to reduce particulate emissions from power plants that burn fossil fuels.

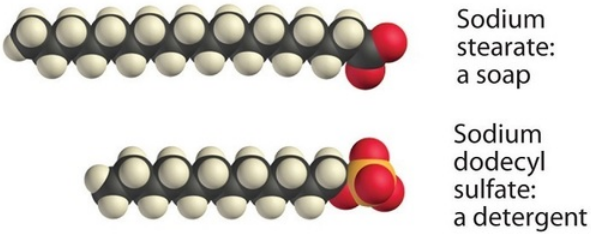
Emulsions

Emulsions are colloids formed by the dispersion of a hydrophobic liquid in water, thereby bringing two mutually insoluble liquids, such as oil and water, in close contact. Various agents have been developed to stabilize emulsions, the most successful being molecules that combine a relatively long hydrophobic “tail” with a hydrophilic “head”:



Bond line drawing of soap, The hydrophobic tail is a long hydrocarbon chain. The hydrophilic heat is a carbon double bonded to an oxygen and single bonded to a negatively charged oxygen.

Examples of such emulsifying agents include soaps, which are salts of long-chain carboxylic acids, such as sodium stearate $[CH_3(CH_2)_{16}CO_2-Na^+]$, and detergents, such as sodium dodecyl sulfate $[CH_3(CH_2)_{11}OSO_3-Na^+]$, whose structures are as follows:



When you wash your laundry, the hydrophobic tails of soaps and detergents interact with hydrophobic particles of dirt or grease through dispersion forces, dissolving in the interior of the hydrophobic particle. The hydrophilic group is then exposed at the surface of the particle, which enables it to interact with water through ion–dipole forces and hydrogen bonding. This causes the particles of dirt or grease to disperse in the wash water and allows them to be removed by rinsing. Similar agents are used in the food industry to stabilize emulsions such as mayonnaise.

A related mechanism allows us to absorb and digest the fats in buttered popcorn and French fries. To solubilize the fats so that they can be absorbed, the gall bladder secretes a fluid called bile into the small intestine. Bile contains a variety of bile salts, detergent-like molecules that emulsify the fats.

Micelles

Detergents and soaps are surprisingly soluble in water in spite of their hydrophobic tails. The reason for their solubility is that they do not, in fact, form simple solutions. Instead, above a certain concentration they spontaneously form micelles, which are spherical or cylindrical aggregates that minimize contact between the hydrophobic tails and water. In a micelle, only the hydrophilic heads are in direct contact with water, and the hydrophobic tails are in the interior of the aggregate (Figure $11.7.4a$).

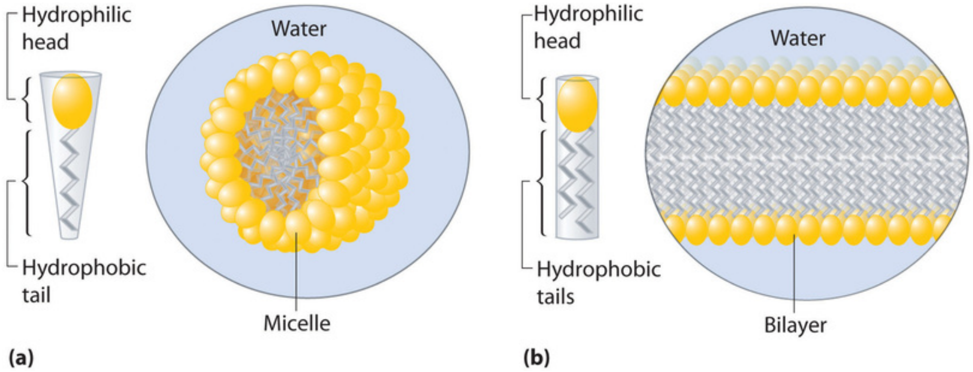
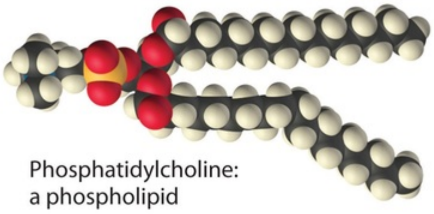


Figure 11.7.4: Micelles and a Phospholipid Bilayer. (a) Soaps and detergents, which contain a single hydrophobic tail on each molecule, form spherical micelles with the intertwined tails in the interior and the hydrophilic head groups on the exterior. (b) Phospholipids, which have two hydrophobic tails, tend to form extended double layers in which the hydrophobic tails are sandwiched between the hydrophilic head groups.

A large class of biological molecules called phospholipids consists of detergent-like molecules with a hydrophilic head and two hydrophobic tails, as can be seen in the molecule of phosphatidylcholine. The additional tail results in a cylindrical shape that prevents phospholipids from forming a spherical micelle. Consequently, phospholipids form bilayers, extended sheets consisting of a double layer of molecules. As shown in Figure $11.7.4b$, the hydrophobic tails are in the center of the bilayer, where they are not in contact with water, and the hydrophilic heads are on the two surfaces, in contact with the surrounding aqueous solution.



A cell membrane is essentially a mixture of phospholipids that form a phospholipid bilayer. One definition of a cell is a collection of molecules surrounded by a phospholipid bilayer that is capable of reproducing itself. The simplest cells are bacteria, which consist of only a single compartment surrounded by a single membrane. Animal and plant cells are much more complex, however, and contain many different kinds of compartments, each surrounded by a membrane and able to carry out specialized tasks.

Summary

A suspension is a heterogeneous mixture of particles of one substance distributed throughout a second phase; the dispersed particles separate from the dispersing phase on standing. In contrast, the particles in a colloid are smaller and do not separate on standing. A colloid can be classified as a sol, a dispersion of solid particles in a liquid or solid; a gel, a semisolid sol in which all of the liquid phase has been absorbed by the solid particles; an aerosol, a dispersion of solid or liquid particles in a gas; or an emulsion, a dispersion of one liquid phase in another. A colloid can be distinguished from a true solution by its ability to scatter a beam of light, known as the Tyndall effect. Hydrophilic colloids contain an outer shell of groups that interact favorably with water, whereas hydrophobic colloids have an outer surface with little affinity for water. Emulsions are prepared by dispersing a hydrophobic liquid in water. In the absence of a dispersed hydrophobic liquid phase, solutions of detergents in water form organized spherical aggregates called micelles. Phospholipids are a class of detergent-like molecules that have two hydrophobic tails attached to a hydrophilic head. A bilayer is a two-dimensional sheet consisting of a double layer of phospholipid molecules arranged tail to tail with a hydrophobic interior and a hydrophilic exterior. Cells are collections of molecules that are surrounded by a phospholipid bilayer called a cell membrane and are able to reproduce themselves.

11.E: Solutions (Exercises)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

Q.1

A student goes to the hospital and has blood work done and the results state that he has a bromide count of $3.17\frac{mg}{dL}$.

a. What is the molar concentration of the students blood?
b. What is the molality of the student's blood if the density of his blood was found to be $1.06\frac{g}{mL}$?
c. How much of the students blood would be require to get $3g$ of bromide?

Solution

The molar mass of bromide is $79.90\frac{g}{mol}$ $1L = 10dL$, $1g = 1000mg$

$$\left(\frac{3.17\ \cancel{mg}}{1\ \cancel{dL}}\right)\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{10\ \cancel{dL}}{1\text{L}}\right)\left(\frac{1\text{mol}}{79.90\ \cancel{g}}\right) = 3.97\times 10^{-4}\ \frac{mol}{L}$$

Assume there is 1L of solution. Modality (m) is calculated by:

$$3.17\text{ x }10^{-2}\ \cancel{g}\left(\frac{1\text{ mol}}{79.90\ \cancel{g}}\right)\left(\frac{1}{1.06\text{ kg}}\right) = 3.74\times 10^{-4}\frac{mol}{kg}$$

If we know that there is $3.17\times10^{-2}g$ of bromide in $1L$ of blood, so all that needs to be done is divide $3g$ by $3.17\times10^{-2}\ \frac{g}{L}$:
Volume of Blood = 94.64 L

Q.5

Given a 3.1416 M aqueous solution of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ with a density of $1.5986\ \frac{\text{g}}{\text{mL}}$. Calculate the molality of this solution, remember that the molar mass of sucrose is $342.297\frac{\text{g}}{\text{mol}}$

Solution

Before we calculate the molality of this solution, don't forget that molarity is just mol/L so we will multiply the molarity of the solution by 1 L to isolate the moles.

$$1.00\ \cancel{L}\ \text{Water} = \frac{3.1416\ mol\ \text{Sucrose}}{1.00\ \cancel{L}\ \text{Water}} = 3.1416\ mol\ \text{Sucrose}$$

Once we have the moles of Sucrose we will multiply it by the molar mass of sucrose in order to find the number of sucrose grams present in the solution:

$$3.1416\ \cancel{mol}\ \text{Sucrose} = \frac{342.297\ g\ \text{Sucrose}}{1.00\ \cancel{mol}\ \text{Sucrose}} = 1075.4\ g\ \text{Sucrose}$$

We next will multiply the density by 1000 mL so as get the number of grams per liter, this way we can find the total grams of the solution and can subtract the sucrose grams from the solution grams to find the grams of water.

$$1000\ \cancel{mL}\ = \frac{1.5986\ g\ \text{SucroseSoln}}{1.00\ \cancel{mL}\ \text{SucroseSoln}} = 1598.6\ g/L\ \text{SucroseSoln}$$

$$\text{Water grams} = [1598.6g\ \text{Sucrose Soln.}] - [1075.4g\ \text{Sucrose}] = 523.2g\ \text{Water}\ = 0.5232\ kg\ \text{Water}$$

Lastly we divide the moles of Sucrose by the kg of water in order to get molality.

$$\frac{3.1416\ mol\ \text{Sucrose}}{0.5232\ kg\ \text{Water}} = 6.005\ molal$$

Q.9

A solution contains 75% of ethanol (C_2H_6O) by mass and the rest is water.

a. What is the density of the solution if there is 15 mol of ethanol per liter of solution?
b. To prepare a 3.5L of 2M ethanol, how many milliliters of the solution is needed?

Solution

a) For easy calculation, assume that there is 1 L of the solution. Using:

$$\text{mol} = \text{molarity} \times \text{volume} \tag{11.E.1}$$

The mol of 15M ethanol in 1L is 15 mol. The molar mass of ethanol is $46.068\frac{g}{mol}$ Using the equation below:

$$\text{ethanol mol} = \frac{\text{mass ethanol}}{\text{ethanol molar mass}} \tag{11.E.2}$$

$$\text{ethanol mass in the solution} = \text{ethanol mol} \times \text{molar mass} = (15mol)(46.068\frac{g}{mol}) = 691.02g \tag{11.E.3}$$

Ethanol is 75% of the solution by mass, therefore:

$$\text{mass of solution} \times 0.75 = \text{mass of ethanol} \tag{11.E.4}$$

$$\text{mass of solution} \times 0.75 = 691.02g \tag{11.E.5}$$

$$\text{mass of solution} = \frac{691.02g}{0.75} = 921.36g \tag{11.E.6}$$

The equation to calculate density is:

$$\text{Density} = \frac{\text{mass}}{\text{volume}} \tag{11.E.7}$$

$$\text{Density} = \frac{921.36g}{1L} = 0.921\frac{g}{ml} \tag{11.E.8}$$

b)To prepare a 3.5L of 2M ethanol;

$$\text{ethanol mol needed} = \text{molarity} \times \text{volume} = (2\,\text{M})(3.5\,\text{L}) = 7\,\text{mol} \tag{11.E.9}$$

$$V_{\text{ethanol needed}} = \frac{\text{mol needed}}{\text{molarity}} = \frac{7\,\text{mol}}{15\,\text{mol}} \times 1\,\text{L} = 0.467\,\text{L} \tag{11.E.10}$$

0.467L of the solution is needed, which is 467mL.

Q.14

Rewrite the following balanced equations as net ionic equations.

a. $H_2SO_4(aq) + 2\,NaOH(aq) \rightarrow 2\,H_2O(l) + Na_2SO_4(aq)$
b. $2\,Na_3PO_4(aq) + 3\,CaCl_2(aq) \rightarrow 6\,NaCl(aq) + Ca_3(PO_4)_2(s)$
c. $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2\,NaCl(aq)$
d. $2\,AgNO_3(aq) + ZnCl_2(aq) \rightarrow 2\,AgCl(s) + Zn(NO_3)_2(aq)$

Solution

a. $2\,H^+(aq) + 2\,OH^-(aq) \longrightarrow 2\,H_2O(l)$
b. $2\,PO_4^{3-}(aq) + 3\,Ca^{2+}(aq) \longrightarrow Ca_3(PO_4)_2(s)$
c. $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$
d. $2\,Ag^{2+}(aq) + Cl^-(aq) \longrightarrow 2\,AgCl(s)$

Q.15

Write the balanced chemical equation for the titration of H_2SO_4 with KOH, then find the volume of a 5.49 M KOH solution needed to neutralize 36.2 g of H_2SO_4 .

Solution

The balanced equation of H_2SO_4 with KOH is:

$$H_2SO_4(aq) + 2\,KOH(aq) \longrightarrow K_2SO_4(aq) + 2\,H_2O(l)$$

Calculate the amount of moles of H_2SO_4 being neutralized:

$$n_{H_2SO_4} = 36.2 \text{ g } H_2SO_4 \times \frac{1 \text{ mol } H_2SO_4}{98.079 \text{ g } H_2SO_4} = 0.369 \text{ mol } H_2SO_4$$

Using stoichiometry to find the amount of moles of KOH needed to neutralize the amount of H_2SO_4 present:

$$n_{KOH} = 0.369 \text{ mol } H_2SO_4 \times \frac{2 \text{ mol KOH}}{1 \text{ mol } H_2SO_4} = 0.738 \text{ mol KOH}$$

Calculate the volume of the 5.49 M KOH solution needed to neutralize the amount of H_2SO_4 present:

$$V_{KOH} = 0.738 \text{ mol KOH} \times \frac{1 \text{ L}}{5.49 \text{ mol KOH}} = 0.134 \text{ L} = 134 \text{ mL}$$

Therefore, approximately 134 mL of the 5.49 M KOH solution is needed to neutralize 36.2 g H_2SO_4.

Q.16

Phosphoric acid is made industrially as a by-product of the extraction of calcium phosphate

$$Ca_3(PO_4)_2 + 6\,HNO_3 + 12\,H_2O \longrightarrow 2\,H_3PO_4 + 3\,Ca(NO_3)_2 + 12\,H_2O$$

What volume of 8.5 M phosphoric acid is generated by the reaction of 4.5 metric tons (4500 kg) of calcium phosphate?

Solution

$$4500\,\text{kg } Ca_3(PO_4)_2 \times \left(\frac{1000\,\text{g}}{1\,\text{kg}}\right) \times \left(\frac{1\,\text{mol}}{310\,\text{g}}\right) \times \left(\frac{2\,H_3PO_4}{1\,Ca_3(PO_4)_2}\right) \times \left(\frac{1\,\text{L}}{8.5\,\text{moles}}\right) = 3415.56\,\text{L } H_3PO_4$$

Q.19

Write a balanced equation for the acid-base reaction that leads to the production of each of the following salts.

a. $BaSO_4$
b. $MgSO_3$
c. $PbSO_4$
d. $AgCl$

Solution

a. $Ba(OH)_2(aq) + H_2SO_4(aq) \rightleftharpoons BaSO_4(s) + 2\,H_2O(l)$
b. $Mg(OH)_2(s) + H_2SO_3(aq) \rightleftharpoons MgSO_3(s) + 2\,H_2O(l)$
c. $Pb(OH)_2(s) + H_2SO_4(aq) \rightleftharpoons PbSO_4(s) + 2\,H_2O(l)$
d. $AgOH(s) + HCl(aq) \rightleftharpoons AgCl(s) + H_2O(l)$

Q.21

Hydrogen selenide is classified as a binary acid that has similar properties as hydrogen sulfide. Write down the balanced equation of hydrogen selenide reacting with the base potassium hydroxide and name the salt product of the reaction.

Solution

When the acid H_2S reacts with the base KOH, the reaction goes as follows:

$$H_2S + 2\,KOH \longrightarrow K_2S + 2\,H_2O$$

Forming potassium sulfide.

Similarly, since H_2Se has similar properties as H_2S, a similar reaction occurs:

$$H_2Se + 2\,KOH \longrightarrow K_2Se + 2\,H_2O$$

Potassium selenide is the salt product of the reaction.

Q.25

A student working with an unknown solution of hydrochloric acid is assigned the task of finding its concentration. The student places a 200.0 mL sample of the solution in a 350.0 mL Erlenmeyer flask and titrates the solution with a 0.1234 M solution of sodium hydroxide, where a phenolphthalein indicator is used to find the endpoint. The endpoint is found to be 31.416 mL, what is the concentration of the original hydrochloric acid solution sample?

Solution

Remember that in titration of a strong acid and base, when the endpoint is reached the number of moles used is equal, so the number of moles of NaOH at the endpoint are equal to that of HCl. Use this information to find moles of NaOH from the concentration and volume used to titrate.

$$\text{Concentration of X} = \frac{\text{moles of X}}{\text{liters of X}}$$

Use dimensional analysis to convert concentration of NaOH to moles using the known amount of volume titrated, in liters:

$$0.031416\ \cancel{\text{liter}}\ \text{NaOH} = \frac{0.1234\ \text{mol NaOH}}{1.00\ \cancel{\text{liter}}\ \text{NaOH}} = 0.003877\ \text{mol}$$

Now because we know that the moles of NaOH are equal to the moles of HCl we simply plug in our calculated moles and known original sample volume, in liters, to find the concentration of HCl:

$$\text{Concentration of HCl} = \frac{0.003877\ \text{mol HCl}}{0.200\ \text{liters HCl}} = 0.019385\ \text{M HCl}$$

The concentration of the original hydrochloric acid solution sample was, therefore, 0.019385 M.

Q.41

The vapor pressure of salicylic acid $C_7H_6O_3$ at 200°C is 0.1598 atm. A 19.0 g sample of ethanol C_2H_6O is dissolved in 60.0 g of salicylic acid. Calculate the vapor pressure of salicylic acid above the resulting solution.

Solution

First find the molar masses of salicylic acid and ethanol. Then use them to compute the chemical amounts of the two in solution.

$$n_{C_2H_6O} = 19.0\ g\ C_2H_6O \times \frac{1\ mol\ C_2H_6O}{46.068\ g\ C_2H_6O} = 0.4124\ mol\ C_2H_6O$$

$$n_{C_7H_6O_3} = 60.0\ g\ C_7H_6O_3 \times \frac{1\ mol\ C_7H_6O_3}{138.121\ g\ C_7H_6O_3} = 0.4344\ mol\ C_7H_6O_3$$

The mole fraction of ethanol in the solution equals

$$X_{C_2H_6O} = \frac{0.4124}{0.4344 + 0.4124} = 0.4870$$

The change in vapor pressure of the salicylic acid due to the presence of of the ethanol is

$$\Delta P_{\mathrm{C_4H_6O_3}} = -X_{\mathrm{C_4H_6O_3}} \times P^{\circ}_{\mathrm{C_4H_6O_3}} = -0.5130 \times 0.1518\, atm = -0.08198$$

The final vapor pressure of the salicylic acid equals its original vapor pressure P° plus the change. This is 0.1598 atm minus 0.08198 atm, which is 0.07782 atm.

Q.43

When 53 mol of an unknown compound was added to 100 g of water, the normal boiling point of water increased to 101.1$^{\mathrm{o}}$C. What is the boiling point elevation constant of water? The compound does not dissociate in solution.

Solution

The relevant relationship here is the colligative property associated with boiling point elevation

$$\Delta T_b = iK_b m \tag{11.E.11}$$

$$\Delta T_b = 101.1^o\, C - 100^o\, C = 1.1^o\, C \tag{11.E.12}$$

Since the compound was told to not dissociation, we know that the van't Hoff factors is 1:

$$i = 1 \tag{11.E.13}$$

$$m = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{53\, mol}{0.100\, kg} = 0.53 \frac{mol}{g} \tag{11.E.14}$$

$$1.1^o C = (1) \times K_b \times (0.53 \frac{mol}{g}) \tag{11.E.15}$$

$$K_b = \frac{1.1^o C}{0.53 \frac{mol}{kg}} = 2.075 \frac{^o C\; kg}{mol} \tag{11.E.16}$$

This problem does not give the correct constant though 0.513:

https://chem.libretexts.org/Referenc...perties/B5%3A_Ebullioscopic_(Boiling_Point_Elevation)_Constants

Q.45

When 5.82 g of uniformly dissociating unknown salt, YX, is dissolved in 100.0 g of water, the boiling point of the water is raised by 0.20°C. When 7.09 g of uniformly dissociating unknown salt, ZX, is dissolved in 200.0 g of water, the boiling point of the water is raised by 0.30°C. Assuming both have a van't hoff factor of 2, identify the elements that X, Y, and Z represent.

Solution

For both salts, one can utilize the boiling point elevation expression (including the van't hoff factor):

$$\Delta T = i \times K_b \times m$$

and by substituting moles solute over mass solvent into the molality, m, one can derive that:

$$n_{\text{salt}} = \frac{\Delta T \times m_{\text{water}}}{i \times K_b}$$

From this we get the moles of each salt present, and can therefore get their molar mass by dividing their mass by moles present. Next, subtracting the heavier salt by the lighter salt will yield the molar mass of X, $\sim 35.5 \frac{\mathrm{g}}{\mathrm{mol}}$. Subtracting this from the molar masses of each salt will then yield Y and Z respectively.

$\Delta T = i \times m \times K_b = 2 \times m \times 0.512 = 0.2,\ \text{m of YX} = 0.1953 \frac{\text{mol}}{\text{kg}};\ m \times 0.1 kg = 0.0195\ \text{mol};\ \frac{5.82}{0.0195} = 298.46\ \frac{\text{g}}{\text{mol}}$

$\Delta T = i \times m \times K_b = 2 \times m \times 0.512 = 0.3,\ m\ of\ \text{ZX} = 0.2930 \frac{\text{mol}}{\text{kg}};\ m \times 0.2 kg = 0.0586\ \text{mol};\ \frac{7.09}{0.0586} = 120.99 \frac{\text{g}}{\text{mol}}$

molar mass difference between Y and Z = $298.46 - 120.99 = 177.47 \frac{\text{g}}{\text{mol}}$

Q.47

Camphor is a useful agent for determining solute's molar mass. Camphor's melting point and K_f are given at $451.55\,\mathrm{K}$ and $37.7\,\frac{\mathrm{K\,kg}}{\mathrm{mol}}$. Find the freezing point of the solution of 0.72 g of glucose is dissolved in the 30.0 g of camphor.

Solution

Since we are evaluating glucose as the solute, $i = 1$.

$$\Delta T = -iK_f m \tag{11.E.17}$$

First find number of moles of glucose in the solution using molar mass.

$$\text{Moles}_{\text{glucose}} = \frac{(0.72g)}{(180.1559\frac{g}{mol})} = 0.0040mol \tag{11.E.18}$$

Molality then can be determined.

$$m = \frac{(0.0040mol)}{(0.030kg)} = 0.13\frac{mol}{kg} \tag{11.E.19}$$

Freezing then can be easily found as such:

$$\Delta T = -iK_f m = -(1)(37.7\frac{^oC\ kg}{mol})(0.13\frac{mol}{kg}) = -4.9^oC \tag{11.E.20}$$

The freezing is $451.55K - 4.9K = 446.65K = 173.5^oC$.

Q.48

It is observed that 2 grams of a non-electrolyte solute dissolved in 100 grams of benzene lowered the freezing point of the solution by 0.40°C compared to pure benzene. Given that the freezing point depression constant of benzene is 5.12 K kg/mol, find the molar mass of the solute. If it is given that the molecular formula of the solute is X_8 where X is an element, what is the formula of the solute?

Solution

$$\Delta T = -ik_f m$$

It is given that

$$\Delta T = 0.40^\circ C \tag{11.E.21}$$

Since the solution is a non-electrolyte, i=1

Hence,

$$\frac{0.40}{K_f} = m$$

$$m = \frac{\frac{2}{\text{Molecular Mass}}}{100\times10^{-3}} = \frac{\frac{2}{\text{Molecular Mass}}}{0.1}$$

Hence, we get

$$\frac{0.40\times0.1}{K_f} = \frac{2}{\text{Molecular Mass}}$$

$$\text{Molecular Mass } = \frac{2K_f}{0.40\times0.1}$$

Hence, the Molecular Mass of the solute is $256\ \frac{g}{mol}$

Since the Molecular Mass of the solute is $256\ \frac{g}{mol}$, we can say that,

$$\text{Molecular Mass of X} = \frac{256}{8} = 32$$

The solute is S_8.

Q.49

At what temperature does the first ice crystals begin to form in a 27% salt (by mass) aqueous solution of NaCl? As the crystallization of water carries on, the remaining solution becomes more concentrated, so what happens to the freezing point of the solution? Given that the freezing point depression constant (K_f) of water is $1.86\,\frac{^oC\,kg}{mol}$.

Solution

$$27\%\ \text{NaCl(aq)} = \frac{27\ g\ \text{NaCl}}{73\ g\ \text{H}_2\text{O}} \tag{11.E.22}$$

$$molality = \frac{27\ g\ \text{NaCl}}{73\ g\ \text{H}_2\text{O}} \times \frac{mol\ \text{NaCl}}{58.44\ g} \times \frac{1000\ g}{1\ kg} = 6.33\ m \tag{11.E.23}$$

$$\Delta T = -i \times m \times K_p = -2 \times 6.33\frac{mol}{kg} \times 1.86\frac{^oC \cdot kg}{mol} = -23.5^oC \tag{11.E.24}$$

The first ice crystal begins to appear at -23.5^oC, as the solution becomes more concentrated, its freezing point decreases further because freezing point depression is a colligative property, so the freezing point of a solution is lower than that of the pure solvent and is directly proportional to the molality of the solute.

Q.50

When homemade ice cream is being made, the temperature ranging downward from -3°C are needed. Ice cubes from a freezer have a temperature of about -12°C, which is cold enough; however, when the ice cream mixture is mixed with the ice cubes, the liquid balances out to 0°C, which is too warm. To obtain a liquid that is cold enough, salt NaCl is dissolved in water and ice is added to the saltwater. The salt lowers the freezing point of the water enough so that it can freeze the liquid inside the ice cream maker. The instruction for the ice cream maker say to add one part salt to 11 parts water (by mass). What is the freezing point of this solution in °C? Assume the NaCl dissociates fully into ions, and that the solution is ideal.

Solution

$$\Delta T_f = -ik_f m \tag{11.E.25}$$

$$\frac{1.00\ g\ \text{NaCl}}{53.5\frac{g}{mol}} = 0.01869\ mol\ \text{NaCl} \tag{11.E.26}$$

$$m = \frac{0.01869\ mol}{11.00g(\frac{1\ kg}{1000\ g})} = 1.699m \tag{11.E.27}$$

$$x - (-12^\circ C) = -(2) \times (1.86\frac{^\circ C}{m}) \times (1.699m) \tag{11.E.28}$$

$$x = -18.32^\circ C \tag{11.E.29}$$

Q.53

A sample of a purified unknown compound is dissolved in toluene, diluting the solvent to a volume of 1.05 mL. The resulting solution has an osmotic pressure of 0.025 atm at 275 K. If the solute has a molar mass of 46.06 g/mol, how many grams of the unknown compound were added?

Solution

$$\Pi = \frac{nRT}{V}$$

and we know $T = 275K$, $R = 0.0821 \dfrac{L\ atm}{mol\ K}$ and Π=0.025 atm

Thus V= 1.05 mL

Since we need V in liters because the units of R are $\dfrac{L\ atm}{mol\ K}$, we use unit conversions:

$$1.05\ mL \times \frac{1L}{1000mL} = 0.00105\ L$$

Plug in the values we know to find n

$$0.025 = \frac{n \times 0.0821 \times 275}{0.00105}$$

$$\frac{0.025 \times 0.00105}{0.0821 \times 275} = n$$

$$n = 1.163 \times 10^{-6}$$

Now that we know number of moles we just have to multiply the number of moles by the molar mass to find grams of substance.

$$(1.163 \times 10^{-6}) \times 46.06844 \frac{g}{mol} = 5.356 \times 10^{-5} g$$

Q.57

An amount of hydrogen gas (H_2) with a partial pressure of 4.6 atm is dissolved in water and this solution is sealed. The Henry's Law constant K for this solution at 25^oC is $7.8 \times 10^{-4} \frac{\mathrm{M}}{\mathrm{atm}}$.

a. How many moles of hydrogen gas will dissolve per liter of water? Assume the density of water is $1.0 \frac{\mathrm{grams}}{\mathrm{cm}^3}$ and has not been affected by the temperature.
b. What will the dissolved gas molecules do if the sealed solution is unsealed?

Solution

a) According to Henry's Law,

$$C = k \times P_{\mathrm{gas}}$$

In this equation, C = concentration of gas (M), k = Henry's Law constant ($\frac{M}{atm}$), and P_{gas} = partial pressure of gas.

So, given k and P_{gas}:

$$C = 7.8 \times 10^{-4} \frac{M}{atm} \times 4.6\ atm$$

$$C = 0.003588 \frac{mol\ \mathrm{H}_2}{L_{\mathrm{water}}}$$

b) The partial pressure of H_2 in the Earth's atmosphere is less than 1 atm. When the solution is unsealed, the H_2 molecules will no longer be under enough pressure to dissolve in water, so they will quickly bubble out of the solution and escape as gas into the surroundings.

Q.59

Propene is a colorless organic compound with a weak but unpleasant smell. However, a company can take advantage of its chemical properties to produce propanol:

$$\mathrm{C_3H_6 + H_2O \longrightarrow CH_3(CH_2)_2OH}$$

- The heat of formation of propene is $20.4 \frac{\mathrm{kJ}}{\mathrm{mol}}$.
- The heat of formation of H_2O is $-241.8 \frac{\mathrm{kJ}}{\mathrm{mol}}$.
- The heat of formation of $CH_3(CH_2)_2OH$ is $-104.6 \frac{\mathrm{kJ}}{\mathrm{mol}}$.

What suggestions can you give to the company regarding the conditions of pressure and temperature that will have a maximum yield of propanol at equilibrium without calculating the actual data?

Solution

$$\Delta H^o_{f(\text{propene})} = 20.4 \frac{kJ}{mol} \tag{11.E.30}$$

$$\Delta H^o_{f(\text{water})} = -241.8 \frac{kJ}{mol} \tag{11.E.31}$$

$$\Delta H^o_{f(\text{CH}_3(\text{CH}_2)_2\text{OH})} = -104.6 \frac{kJ}{mol} \tag{11.E.32}$$

$$\Delta H^o = \Delta H^o_{f(\text{CH}_3(\text{CH}_2)_2\text{OH})} - \Delta H^o_{f(\text{propene})} - \Delta H^o_{f(\text{water})} \tag{11.E.33}$$

$$\begin{aligned} &= -104.6 \frac{kJ}{mol} - (-241.8 \frac{kJ}{mol}) - 20.4 \frac{kJ}{mol} \qquad (11.E.34) \\ &= 116.8 \frac{kJ}{mol} > 0 \end{aligned}$$

It is an endothermic reaction. As a result, a higher temperature is required to maximize the yield of product.

Also, according to the ideal gas law, because the moles of gas are proportional to the volume, and the volume is inverse proportional to the pressure; a higher pressure is required to maximize the yield of product.

Q.61

Suppose heptane and octane form an ideal solution. At $20.0\,^\circ\text{C}$, pure heptane has a vapor pressure of $\text{P}_1{}^\circ = 0.0562\ \text{atm}$ while pure octane has a vapor pressure of $\text{P}_2{}^\circ = 0.0145\ \text{atm}$. What is the mole fraction of heptane vapor over a solution of heptane and octane if the solution contained $0.300\ \text{mol}$ heptane and $0.700\ \text{mol}$ octane?

Solution

Since we have been told to assume the solution is ideal, we can use Raoult's law to obtain the partial pressures of heptane and octane, respectively.

$$P_{\text{heptane}} = \left(\frac{0.300\ \text{mol}}{0.300\ \text{mol} + 0.700\ \text{mol}}\right) \times (0.0562\ \text{atm}) = 0.01686\ \text{atm}$$

$$P_{\text{octane}} = \left(\frac{0.700\ \text{mol}}{0.300\ \text{mol} + 0.700\ \text{mol}}\right) \times (0.0145\ \text{atm}) = 0.01015\ \text{atm}$$

Using the relationship between partial pressure and mole fraction, we can obtain the mole fraction of heptane over the solution. Partial pressure and mole fraction can be related through the ideal gas law $P = n\frac{RT}{V}$. Which shows that under constant temperature and pressure, pressure and number of moles are directly related.

$$\chi_{\text{heptane}} = \left(\frac{0.01686\ \text{atm}}{0.01686\ \text{atm} + 0.01015\ \text{atm}}\right) = 0.624$$

Q.63

At 50^{o}C, benzene (C_6H_6) has a vapor pressure of 42.5 kPa and isobutene (C_3H_8) has a vapor pressure of 0.83 torr. When 10.0 g of benzene and 30 g of isobutene are mixed in a solution, they form a nearly ideal solution.

a. Calculate the mole fraction of benzene in the solution.
b. What is the total vapor pressure above the solution in kPa at 50^{o}C ?
c. Calculate the mole fraction of isobutene that exists above the solution in the vapor phase.

Solution

The mole fraction is equal to:

$$\left(\frac{X_A\,mol}{X_A+X_B\,mol}\right)$$

Use dimensional analysis to convert grams to moles:

$$(10.0\ \cancel{g\,\mathrm{C_6H_6}})\left(\frac{1\ mol}{78.108\ \cancel{g\,\mathrm{C_6H_6}}}\right)=0.128\ mol$$

$$(30.0\ \cancel{g\,\mathrm{C_3H_8}})\left(\frac{1\ mol}{44.094\ \cancel{g\,\mathrm{C_3H_8}}}\right)=0.680\ mol$$

Let:

$X_A =$ the moles of $\mathrm{C_6H_6} = 0.128\ mol$, $X_B =$ the moles of $\mathrm{C_3H_8} = 0.680\ mol$,

$$\chi_B=\frac{0.0929\ kPa}{6.81\ kPa}=0.0136$$

Plug into the equation and solve:

$$\left(\frac{0.128\ mol}{0.128+0.680\ mol}\right)=0.158$$

b) Since the problem states that the result of mixing the two solutions is nearly ideal, we can assume an ideal solution is formed and use Raoult's Law and we can choose to keep pressure in units of kPa OR torr.

It's Raoult's Law:

$P_A=\chi_A\times P_A^o$

Here we have chosen to use units of kPa:

$$P_{\mathrm{C_6H_6}}=\chi_{\mathrm{C_6H_6}}\times P^o_{\mathrm{C_6H_6}}$$

$$P_{\mathrm{C_6H_6}}=0.158\times 42.5\ kPa=6.72\ kPa$$

To convert torr to kPa:

$$(0.83\ \cancel{torr})\left(\frac{0.133\ kPa}{1\ \cancel{torr}}\right)=0.1104\ kPa$$

$$P_{\mathrm{C_3H_8}}=\chi_{\mathrm{C_3H_8}}\times P^o_{\mathrm{C_3H_8}}$$

$$P_{\mathrm{C_3H_8}}=0.842\times 0.1104\ kPa=0.0929\ kPa$$

Then we add these up to find the total pressure:

$$P_{\text{Total}}=\chi_A P_A^o+\chi_B P_B^o$$

$$P_{\text{Total}}=6.72\ kPa+0.0929\ kPa\ =6.81\ kPa$$

c) To find the mole fraction of isobutene **only** in the vapor phase, we can use partial pressure to represent the amount of gas, becase in mixed gas $n \propto p$:

$$\chi_{\text{isobutene}}=\frac{n_{\text{isobutene}}}{n_{\text{tot}}}=\frac{P_{\text{isobutene}}}{P_{\text{tot}}}=\frac{0.83\,\text{torr}}{6.81\,\text{kPa}}=0.0162$$

Q.65

A solution is prepared by mixing 2g of $\mathrm{CaCl_2(s)}$, 2g of $\mathrm{MgCl_2(s)}$, and 3g of $\mathrm{MnO_2(s)}$ in enough water to make a total volume of 150 mL. Calculate the concentration of chlorine in the solution in grams per liter.

Solution

$m_{\mathrm{Cl}} = 2g\,\mathrm{CaCl_2}\left(\frac{2(35.5g\,\mathrm{Cl})}{110.98g\,\mathrm{CaCl_2}}\right) + 2g\,\mathrm{MgCl_2}\left(\frac{2(35.5g\,\mathrm{Cl})}{95.12g\,\mathrm{MgCl_2}}\right)$

$m_{\mathrm{Cl}} = 2.77g\,\mathrm{Cl}$

mass of chlorine per liter: $\frac{2.77g\,\mathrm{Cl}}{150\times10^{-3}L} = 18.5\frac{g}{L}$

Q.69

Chromium ion, $\mathrm{Cr^{2+}}$, is a good reducing agent, often being itself turned into $\mathrm{Cr^{3+}}$. Suppose that 10 mL of 0.1 M $\mathrm{Cr(OH)_2}$ was needed to reduce completely an 0.05 grams of unknown substance X.

a. If each molecule of X accept just one electron, what is the molecular weight of X?
b. If each molecule of X accept five electrons, what is the molecular weight of X?

Solution

(a) Number of moles of $\mathrm{Cr(OH)_2}$ used = $M \times V$

$= 0.1 \times 10\text{ mL} = 1\text{ mmol} = 10^{-3}$ moles

Since only one mole of X was used for every mole of Chromium Hydroxide, the number of moles reacted are equal.

$\frac{\text{Mass}}{\text{Molar mass}}$ = number of moles, hence for X,

$\frac{0.05\text{ g}}{(0.01\text{L}\times0.1\text{M})} = 50\frac{\text{g}}{\text{mol}}$

(b) $\frac{0.05\text{ g}}{(0.01\text{L}\times0.1\text{M}\times5)} = 10\frac{\text{g}}{\text{mol}}$

Q.71

A 0.200 g sample of chloride with unknown purity was dissolved in 200 mL of water was then titrated with $\mathrm{AgNO_3}$ solution with a molarity of 0.1 M. After the titration it was determined that 28 mL of $\mathrm{AgNO_3}$ was required to fully titrate the sample of chloride. What's the mass percent of chloride in the original dry sample?

Solution

First write the precipitation reaction:

$$\mathrm{Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)}$$

Next we need to determine the amount of moles of Ag used during the titration:

$$\text{mol Ag}^+ = 28\,\cancel{mL}\left(\frac{1\,\cancel{L}}{1000\,\cancel{mL}}\right)\left(\frac{0.1\text{ mol}}{1\,\cancel{L}}\right) = 2.80\times10^{-3}\text{ mol Ag}^+$$

Now that we know the amount of moles of Ag reacted because Ag and Cl combine at a one to one ration we can find the mass of Cl used:

$$\text{mass Cl}^- = 2.80\times10^{-3}\,\cancel{mol}\left(\frac{35.45\text{ g}}{1\,\cancel{mol}}\right) = 9.92\times10^{-2}\text{ g Cl}^-$$

Now that we know the mass of Cl in the unknown we can calculate the mass percent:

$$100\%\left(\frac{0.0992\text{ g}}{0.2\text{g}}\right) = 49.63\%$$

Q.73

At 20°C, the vapor pressure of pure water is 17.5 mmHg. When 110 g of a substance X_y is dissolved in 500 g of water, the vapor pressure of the solution is 15.0 mmHg. Given that this substance has a molecular mass of 12.011 g/mol, what is the molecular formula of this substance X_y. (i.e. what is the number value of subscript y).

Solution

For this question, we can use Raoult's Law

$$P_{\text{solution}} = \chi_{\text{solvent}} \times P^\circ{}_{\text{solvent}}$$

First, we plug in the known values of the pressure of the solution and the pressure of the pure solvent, water, to find the mole fraction.

$$15.0 \text{ mmHg} = \chi_{\text{solvent}} \times 17.5 \text{ mmHg}$$

$$\chi_{\text{solvent}} = 0.8571$$

Next, we can calculate the the number of moles of the solvent from its mass and molecular weight.

$$\text{Moles of solvent} = 500 \text{ g} \times \frac{1}{18.015 \text{ g/mol}} = 27.75 \text{ moles}$$

Next, we can calculate the moles of the solute from the mole fraction of the solvent

$$0.8571 = \frac{27.75 \text{ moles}}{27.75 \text{ moles } + \text{ moles of } X_y}$$

$$\text{moles of } X_y = 4.63 \text{ moles}$$

From here, we can calculate the molecular formula of the substance by dividing the amount of grams per mole used in the solution by the molecular mass of the substance.

$$\frac{110 \text{ g}}{4.63 \text{ moles}} = 23.76 \text{ g/mol}$$

$$(23.76 \text{ g/mol}) \times (\frac{1}{12.011 \text{ g/mol}}) = 1.98$$

$$1.98 \approx 2$$

Thus, the molecular formula of our substance is X_2.

Q.81

The cell membrane of a plant cell is permeable to water. In a salt solution, the plant cells shrivel (lose water) when the concentration is high, and swell (take up water) when the concentration is low. Scientists perform an experiment at 30°C, where an aqueous solution of NaCl with a freezing point of -0.028°C is used to water the plant cells. This causes the plant cells to neither swell nor shrink indicating that the osmotic pressure of the plant cell contents is equal to that of the NaCl solution. Assuming the molarity and molality of the plant cell contents are equal, calculate the osmotic pressure of the solution inside the plant cells. The K_f for the solution is $1.86 \frac{\text{K kg}}{\text{mol}}$.

Solution

Plug in the given values into the equation for freezing point depression to solve for the molality of the solution

$$\Delta T_f = -K_f m$$

$$-0.0218 = -1.86 K \cdot kg \cdot mol^{-1} m$$

$$m = 0.015 \frac{kg}{mol}$$

Because the plant cell neither swells nor shrinks, the molality of the solution is equivalent to the molality of the plant cell contents. According to the question, assume the molarity and molality are equal so concentration

$$c = 0.15 M$$

Use the following equation to calculate for the osmotic pressure, π.

$$\begin{aligned}\pi &= cRT \\ &= (0.15M)(0.08206\frac{L\ atm}{mol\ K})(303.15K) \\ &= 0.374atm\end{aligned}$$

Q.83

Jim loves the smell of grass. He loves it so much that he frequently sniffs the fumes from 1-Hexanol, which is a chemical compound that is known to smell like grass trimmings. Because of his love, he decides to make his garage into a "gas den", and aimed to have 60% of the air in it as 1-Hexanol gas. He achieves this by filling a pool with a mixture of 1-Hexanol and Water. Assume that the air in the "gas den" consists of only the fumes from this mixture. If the pool has 10000L of water in it, how many litres of 1-Hexanol does he need? Use Henry's Law to determine this amount.

Relevant Information:

1-Hexanol:

- Density: $814\frac{kg}{m^3}$
- Molar mass: $107.1748\frac{g}{mol}$
- Henry's Law Constant: $64\frac{molal}{bar}$

Water:

- Density: $1000\frac{kg}{m^3}$

Solution

This problem asks for the amount, in litres, of 1-Hexanol that is required to make Jim's dreams come true. The information given is the density of 1-Hexanol and its molar mass, but since they don't have very much to do with pressure, they can be set aside for now. The question explicitly mentions that Henry's Law should be used, so start be identifying what Henry's Law actually does:

$$C = kP$$

Where C is concentration, k is Henry's Law constant, and P is partial pressure. The question gives out the fact that Jim wants the air in his garage to be 60% 1-Hexanol vapor. Remember the total pressure of air is 1 atm ≈ 1 bar (ignore the error here). Therefore, the partial pressure of 1-hexanol is $1\text{ bar} \times 60\% = 0.6\text{ bar}$. The Henry's Law constant is also provided, and by plugging those two in, the concentration of 1-Hexanol in the desired "solution" (more accurately, giant pool of chemicals) is found. This process is shown below:

$$C = kP = (64\frac{molal}{bar}) \times 0.6\text{ bar} = 38.4$$

This concentration, from the units of k, is in mo*lality*, which is $\frac{mol_{\text{solute}}}{kg_{\text{solvent}}}$. Now all that is left is to convert molality to litres. By utilizing the molar mass of 1-Hexanol:

$$38.4\frac{mol_{\text{solute}}}{kg_{\text{solvent}}} \times 107.1748\frac{g}{mol} \approx 4115.51\frac{g_{\text{solute}}}{kg_{\text{solvent}}}$$

We know that the solvent is water, and that water has a density of $1000\frac{kg}{m^3}$. Also, the conversion rate of m^3 to L is 1:1000. Therefore, the equation can be solved as follows.

$$4115.51\frac{g_{\text{solute}}}{kg_{\text{solvent}}} \times 1000\frac{kg_{H_2O}}{m^3} \times \frac{m^3}{1000\ L_{H_2O}} \approx 4115.51\frac{g_{\text{solute}}}{L_{\text{solvent}}}$$

We now have the value for how many grams of solute (1-Hexanol) there should be per litre of solvent. simply divide this value by the density to obtain litres of 1-Hexanol per litre of water. Multiply this number by the amount of water in the pool to get the desired amount of solute that is needed for the solution! (note that the density was converted to $\frac{g}{L}$,

$$4115.51\frac{g_{\text{solute}}}{L_{\text{solvent}}} \div \left(814000\frac{g_{\text{1-hexanol}}}{L}\right) \times 10000L_{\mathrm{H_2O}} = 50.56\,\mathrm{L}$$

~~Therefore, Jim needs 50,560L of 1-Hexanol to put in his pool. That's going to take a big pool!~~

Therefore, Jim needs 50.56L of 1-Hexanol to put in his pool.

Please note that, while various units do appear in the conversions, $\mathrm{H_2O}$ can be considered as solute and 1-Hexanol as the solvent, so the units can cancel.

Abstract: Utilize henry's law to find concentration (molality). From that, convert molality to g_{solute} to L_{solute}.

Q.87

A 3.5 gram sample is decomposed into a compound containing nitrogen, hydrogen, and oxygen, together creating 4.00 g of $\mathrm{NO_2}$ and 7.00 g of $\mathrm{H_2O}$. The molar mass of the sample is $78.5\,\frac{\mathrm{g}}{\mathrm{mol}}$. Find the molecular formula of this sample.

Solution

First, the moles of each Nitrogen, Hydrogen, and Oxygen in solution are calculated:

$$mol_N = 4g\,\mathrm{NO_2} \times \left(\frac{1\ mol\ \mathrm{NO_2}}{46.005\frac{g}{mol}}\right) \times \left(\frac{1\ mol\ N}{1\ mol\ \mathrm{NO_2}}\right) = 0.0869\ mol$$

$$mass_N = (14.00\frac{g}{mol})(0.0869mol) = 1.2172g\,\mathrm{N}$$

$$mol_H = 7g\,\mathrm{H_2O} \times \left(\frac{1\ mol\ H_2O}{18.02\frac{g}{mol}}\right) \times \left(\frac{2\ mol\ H}{1\ mol\ \mathrm{H_2O}}\right) = 0.7769\ mol$$

$$mass_H = (1.01\frac{g}{mol})(0.7769mol) = 0.7847g\,\mathrm{H}$$

From these values, moles of O can be calculated to be:

$$3.5\ gram\ sample = grams_N + grams_H + grams_O$$

$$3.5 = 1.2172g + 0.7847g + grams_O$$

$$grams_O = 1.4981g$$

$$mol_O = \frac{1.4981g}{15.9994\frac{g}{mol}} = 0.0936\ mol$$

The mole values for each element create a ratio of $\mathrm{H_{0.7769}N_{0.0869}O_{0.0936}}$, creating an empirical formula $\mathrm{H_9NO}$

From here, the molecular formula can be established using the molar mass:

$$\text{Empirical formula mass} = 9(1.01\frac{g}{mol\ H}) + (14.00\frac{g}{mol\ N}) + (15.9994\frac{g}{mol\ O})$$

$$\text{Empirical formula mass} = 39.0894\frac{g}{mol}$$

$$\text{Sample Mass} = 78.5\frac{g}{mol}$$

$$\frac{78.5\frac{g}{mol}}{39.084\frac{g}{mol}} = 2.00$$

$$2(\mathrm{H_9NO}) = \mathrm{H_{18}N_2O_2} = \text{Molecular Formula}$$

Q.87

5 grams of a substance containing hydrogen, carbon and oxygen were fully combusted and produced 3.00 grams of $\mathrm{H_2O}$ and 7.33 grams of $\mathrm{CO_2}$. When 10.64 grams of the substance was mixed with 0.5 kg of water, the freezing point was found to decrease by 0.0605°C. What is the substance?

Solution

The generic equation for this reaction is

$$\mathrm{C_xH_yO_z + O_2 \longrightarrow H_2O + CO_2}$$

The molar masses of carbon, hydrogen, and oxygen are 12.01 g/mol, 1.008 g/mol, and 16.00 g/mol respectively. Therefore the molar masses of water and carbon dioxide are $18.016\frac{g}{mol}$ and $44.01\frac{g}{mol}$ These values can be used to determine the mass percent of hydrogen in water

$$\frac{2(1.008)\ \frac{g}{mol}}{18.016\ \frac{g}{mol}} \times 100 = 11.2\%$$

And the mass percent of carbon in carbon dioxide

$$\frac{12.01\ \frac{g}{mol}}{44.01\ \frac{g}{mol}} \times 100 = 27.3\%$$

The mass percents can be used to determine the amount of hydrogen and carbon are present.

$$3.00\ g \times 0.112 = 0.336\ g \text{ of Hydrogen}$$

$$7.33\ g \times 0.273 = 2.001\ g \text{ of Carbon}$$

By subtracting the masses of Carbon and Hydrogen from the original mass of the substance, the mass of oxygen present in the substance can be found

$$5\ g - (0.336\ g + 2.001\ g) = 2.663\ g \text{ of Oxygen}$$

By dividing the masses present by the molar mass, the amount of moles of each element can be determined

$$\frac{0.112\ g}{1.008\ \frac{g}{mol}} = 0.333\ mol \text{ of Hydrogen}$$

$$\frac{2.001\ g}{12.01\ \frac{g}{mol}} = 0.167\ mol \text{ of Carbon}$$

$$\frac{2.663\ g}{16.00\ \frac{g}{mol}} = 0.166\ mol \text{ of Oxygen}$$

By looking at the amount of moles of each element, it can be noticed that there are equal amounts of carbon and oxygen and twice as much hydrogen as carbon or oxygen. Therefore the ratio of $\mathrm{C:H:O}$ in the substance is 1 : 2 : 1. However, the molar mass of the substance remains unknown, but it can be found using the information about the freezing point depression.

From the formula for freezing point depression

$$\Delta T = -i \times k_f \times m$$

$$-0.0605^\circ C = -1 \times 0.512^\circ C\ m^{-1} \times m$$

$$m = \frac{0.0605^\circ C}{0.512\frac{^\circ C}{m}} = 0.118\ \frac{mol}{kg}$$

By multiply by the mass of solvent (water), we can determine the amount of moles that was dissolved in the water

$$0.118\ \frac{mol}{kg} \times 0.5\ kg = 0.059\ mol$$

The last step in finding the molar mass of the substance is to divide the mass dissolved by the moles dissolved

$$\frac{10.64\ g}{0.059\ mol} = 180.3\ \frac{g}{mol}$$

Now we can find the formula of the substance. The first step is to find the number of moles of the substance combusted

$$\frac{5\ g}{180.3\ \frac{g}{mol}} = 0.0277\ mol$$

We can compare this to the number of carbon moles combusted to determine the number of carbon atoms per molecule of the substance

$$\frac{0.167\ g\,\text{of Carbon}}{0.0277\ mol} = 6\ \text{Carbon atoms}$$

When we apply the number of carbon atoms to the ratio of elements found earlier, the chemical formula comes to be $C_6H_{12}O_6$ which is glucose.

Answer: Glucose

SECTION OVERVIEW

Unit 4: Equilibrium in Chemical Reactions

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

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Chemical equilibrium is a state in which the rate of the forward reaction equals the rate of the backward reaction. In other words, there is no net change in concentrations of reactants and products. This kind of equilibrium is also called dynamic equilibrium and can be used in a wide range of processes including both chemical and physical changes.

12: Thermodynamic Processes and Thermochemistry

13: Spontaneous Processes and Thermodynamic Equilibrium

14: Chemical Equilibrium

15: Acid–Base Equilibria

16: Solubility and Precipitation Equilibria

17: Electrochemistry

CHAPTER OVERVIEW

12: Thermodynamic Processes and Thermochemistry

This chapter introduces you to **thermochemistry**, a branch of chemistry that describes the energy changes that occur during chemical reactions. In some situations, the energy produced by chemical reactions is actually of greater interest to chemists than the material products of the reaction. For example, the controlled combustion of organic molecules, primarily sugars and fats, within our cells provides the energy for physical activity, thought, and other complex chemical transformations that occur in our bodies. Similarly, our energy-intensive society extracts energy from the combustion of fossil fuels, such as coal, petroleum, and natural gas, to manufacture clothing and furniture, heat your home in winter and cool it in summer, and power the car or bus that gets you to class and to the movies.

12.1: Systems, States, and Processes

Learning Objectives

- To understand the concept of energy and its various forms.
- To know the relationship between energy, work, and heat.

Because energy takes many forms, only some of which can be seen or felt, it is defined by its effect on matter. For example, microwave ovens produce energy to cook food, but we cannot see that energy. In contrast, we can see the energy produced by a light bulb when we switch on a lamp. In this section, we describe the forms of energy and discuss the relationship between energy, heat, and work.

Forms of Energy

The forms of energy include thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy (Figure 12.1.1). Thermal energy results from atomic and molecular motion; the faster the motion, the greater the thermal energy. The temperature of an object is a measure of its thermal energy content. Radiant energy is the energy carried by light, microwaves, and radio waves. Objects left in bright sunshine or exposed to microwaves become warm because much of the radiant energy they absorb is converted to thermal energy. Electrical energy results from the flow of electrically charged particles. When the ground and a cloud develop a separation of charge, for example, the resulting flow of electrons from one to the other produces lightning, a natural form of electrical energy. Nuclear energy is stored in the nucleus of an atom, and chemical energy is stored within a chemical compound because of a particular arrangement of atoms.

(a) Thermal energy (b) Radiant energy

(c) Electrical energy (d) Nuclear energy (e) Chemical energy

Figure 12.1.1: Forms of Energy. (a) *Thermal energy* results from atomic and molecular motion; molten steel at 2,000°C has high thermal energy. (b) *Radiant energy* (e.g., from the sun) is the energy in light, microwaves, and radio waves. (c) Lightning is an example of *electrical energy*, which is due to the flow of electrically charged particles. (d) *Nuclear energy* is released when particles in the nucleus of the atom are rearranged. (e) *Chemical energy* results from the particular arrangement of atoms in a chemical compound; the heat and light produced in this reaction are due to energy released during the breaking and reforming of chemical bonds. (CC BY-SA-NC; anonymous)

Electrical energy, nuclear energy, and chemical energy are different forms of potential energy (PE), which is energy stored in an object because of the relative positions or orientations of its components. A brick lying on the windowsill of a 10th-floor office has a great deal of potential energy, but until its position changes by falling, the energy is contained. In contrast, kinetic energy (KE) is energy due to the motion of an object. When the brick falls, its potential energy is transformed to kinetic energy, which is then transferred to the object on the ground that it strikes. The electrostatic attraction between oppositely charged particles is a form of potential energy, which is converted to kinetic energy when the charged particles move toward each other.

Energy can be converted from one form to another (Figure 12.1.2) or, as we saw with the brick, transferred from one object to another. For example, when you climb a ladder to a high diving board, your body uses chemical energy produced by the combustion of organic molecules. As you climb, the chemical energy is converted to *mechanical work* to overcome the force of gravity. When you stand on the end of the diving board, your potential energy is greater than it was before you climbed the ladder: the greater the distance from the water, the greater the potential energy. When you then dive into the water, your potential energy is converted to kinetic energy as you fall, and when you hit the surface, some of that energy is transferred to the water, causing it to splash into the air. Chemical energy can also be converted to radiant energy; one common example is the light emitted by fireflies, which is produced from a chemical reaction.

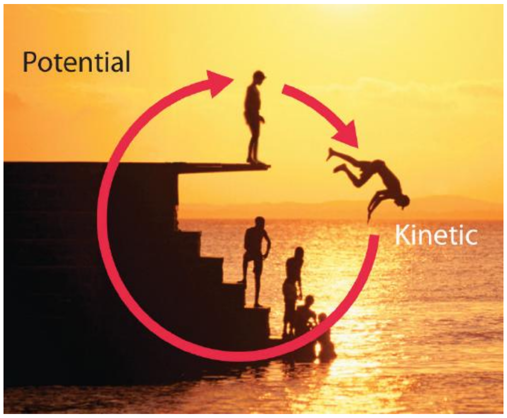


Figure 12.1.2: Interconversion of Forms of Energy. When a swimmer steps off the platform to dive into the water, potential energy is converted to kinetic energy. As the swimmer climbs back up to the top of the diving platform, chemical energy is converted to mechanical work. (CC BY-SA-NC; anonymous)

Although energy can be converted from one form to another, *the total amount of energy in the universe remains constant*. This is known as the **law of conservation of energy**: *Energy cannot be created or destroyed.*

Kinetic and Potential Energy

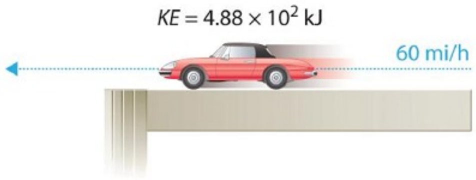
The kinetic energy of an object is related to its mass m and velocity v:

$$KE = \frac{1}{2}mv^2 \tag{12.1.1}$$

For example, the kinetic energy of a 1360 kg (approximately 3000 lb) automobile traveling at a velocity of 26.8 m/s (approximately 60 mi/h) is

$$\begin{aligned} KE &= \frac{1}{2}(1360\,kg)(26.8\,ms)^2 \\ &= 4.88 \times 10^5 g \cdot m^2 \end{aligned} \tag{12.1.2}$$

Because all forms of energy can be interconverted, energy in any form can be expressed using the same units as kinetic energy. The SI unit of energy, the joule (J), is named after the British physicist James Joule (1818–1889), an early worker in the field of energy, is defined as 1 kilogram·meter^2/second^2 (kg·m^2/s^2). Because a joule is such a small quantity of energy, chemists usually express energy in kilojoules (1 kJ = 10^3 J). For example, the kinetic energy of the 1360 kg car traveling at 26.8 m/s is 4.88 × 10^5 J or 4.88 × 10^2 kJ. It is important to remember that *the units of energy are the same regardless of the form of energy*, whether thermal, radiant, chemical, or any other form. Because heat and work result in changes in energy, their units must also be the same.



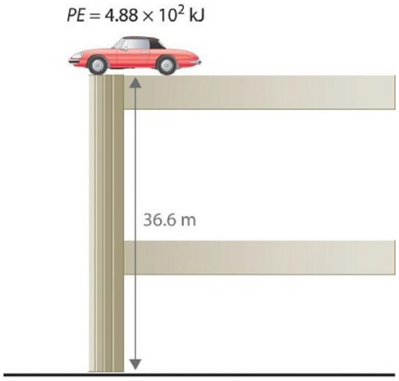
To demonstrate, let's calculate the potential energy of the same 1360 kg automobile if it were parked on the top level of a parking garage 36.6 m (120 ft) high. Its potential energy is equivalent to the amount of work required to raise the vehicle from street level to the top level of the parking garage, which is

$$w = F\,d. \tag{12.1.3}$$

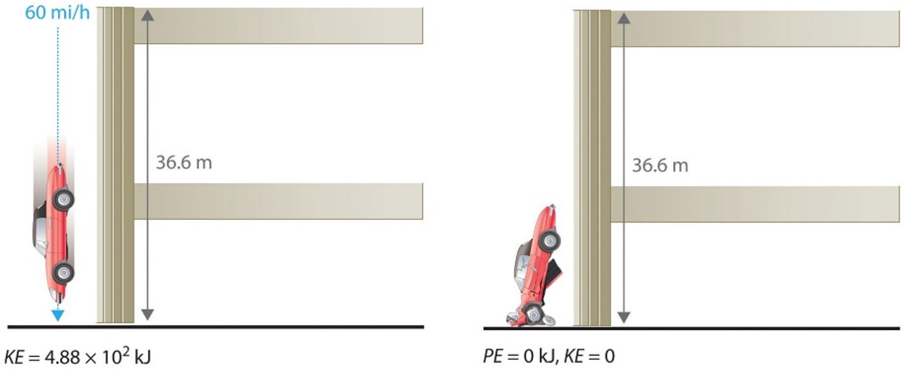
The force (F) exerted by gravity on any object is equal to its mass (m, in this case, 1360 kg) times the acceleration (a) due to gravity (g, 9.81 m/s^2 at Earth's surface). The distance (d) is the height (h) above street level (in this case, 36.6 m). Thus the potential energy of the car is as follows:

$$\begin{aligned} PE &= F\,d = m\,a\,d = m\,g\,h \\ &= (1360\;Kg)\left(\frac{9.81\;m}{s^2}\right)(36.6\;m) \\ &= 4.88 \times 10^5\;\frac{Kg \cdot m^2}{s^2} \\ &= 4.88 \times 10^5 J = 488\;kJ \end{aligned} \tag{12.1.4}$$

The units of potential energy are the same as the units of kinetic energy. Notice that in this case the potential energy of the stationary automobile at the top of a 36.6 m high parking garage is the same as its kinetic energy at 60 mi/h.



If the vehicle fell from the roof of the parking garage, its potential energy would be converted to kinetic energy, and it is reasonable to infer that the vehicle would be traveling at 60 mi/h just before it hit the ground, neglecting air resistance. After the car hit the ground, its potential and kinetic energy would both be zero.



Potential energy is usually defined relative to an arbitrary standard position (in this case, the street was assigned an elevation of zero). As a result, we usually calculate only differences in potential energy: in this case, the difference between the potential energy of the car on the top level of the parking garage and the potential energy of the same car on the street at the base of the garage.

Units of Energy

The units of energy are the same for all forms of energy. Energy can also be expressed in the non-SI units of calories (cal), where 1 cal was originally defined as the amount of energy needed to raise the temperature of exactly 1 g of water from 14.5 °C to 15.5 °C.We specify the exact temperatures because the amount of energy needed to raise the temperature of 1 g of water 1 °C varies slightly with elevation. To three significant figures, however, this amount is 1.00 cal over the temperature range 0 °C–100 °C. The name is derived from the Latin *calor*, meaning "heat." Although energy may be expressed as either calories or joules, calories were defined in terms of heat, whereas joules were defined in terms of motion. Because calories and joules are both units of energy, however, the calorie is now defined in terms of the joule:

$$1\ cal \equiv 4.184\ J \quad \text{(exactly)} \tag{12.1.5}$$

$$1\ J = 0.2390\ cal \tag{12.1.6}$$

In this text, we will use the SI units—joules (J) and kilojoules (kJ)—exclusively, except when we deal with nutritional information.

✓ Example 12.1.1: Kinetic Energy of Baseballs

a. If the mass of a baseball is 149 g, what is the kinetic energy of a fastball clocked at 100 mi/h?
b. A batter hits a pop fly, and the baseball (with a mass of 149 g) reaches an altitude of 250 ft. If we assume that the ball was 3 ft above home plate when hit by the batter, what is the increase in its potential energy?

Given

- mass and velocity or height

Asked for

- kinetic and potential energy

Strategy

Use Equation 12.1.1 to calculate the kinetic energy and Equation 12.1.4 to calculate the potential energy, as appropriate.

Solution

a. The kinetic energy of an object is given by $\frac{1}{2}mv^2$ In this case, we know both the mass and the velocity, but we must convert the velocity to SI units:

$$\begin{aligned} v &= \left(\frac{100\ \cancel{mi}}{1\ \cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.61\ \cancel{km}}{1\ \cancel{mi}}\right)\left(\frac{1000\ m}{1\ \cancel{km}}\right) \\ &= 44.7\ m/s \end{aligned}$$

The kinetic energy of the baseball is therefore (via Equation 12.1.1)

$$\begin{aligned} KE &= \frac{1}{2} 149\ \cancel{g} \left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{44.7\ m}{s}\right)^2 \\ &= 1.49 \times 10^2\ \frac{kg \cdot m^2}{s^2} \\ &= 1.49 \times 10^2\ J \end{aligned}$$

b. The increase in potential energy is the same as the amount of work required to raise the ball to its new altitude, which is (250 − 3) = 247 feet above its initial position. Thus

$$\begin{aligned} PE &= 149\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{9.81\ m}{s^2}\right)\left(247\ \cancel{ft}\right)\left(\frac{0.3048\ m}{1\ \cancel{ft}}\right) \\ &= 1.10 \times 10^2\ \frac{kg \cdot m^2}{s^2} \\ &= 1.10 \times 10^2\ J \end{aligned}$$

Exercise 12.1.1

a. In a bowling alley, the distance from the foul line to the head pin is 59 ft and 10 $\frac{13}{16} in.$ (18.26 m). If a 16 lb (7.3 kg) bowling ball takes 2.0 s to reach the head pin, what is its kinetic energy at impact? (Assume its speed is constant.)
b. What is the potential energy of a 16 lb bowling ball held 3.0 ft above your foot?

Answer a

3.10×10^2 J

Answer b

65 J

Systems and Surroundings

To study the flow of energy during a chemical reaction, we need to distinguish between a system, the small, well-defined part of the universe in which we are interested (such as a chemical reaction), and its surroundings, the rest of the universe, including the container in which the reaction is carried out (Figure 12.1.3). In the discussion that follows, the mixture of chemical substances that undergoes a reaction is always the system, and the flow of heat can be from the system to the surroundings or vice versa.

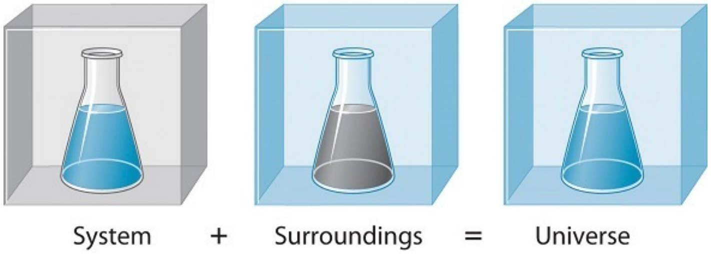


Figure 12.1.3: A System and Its Surroundings. The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out. (CC BY-SA-NC; anonymous)

Three kinds of systems are important in chemistry. An open system can exchange both matter and energy with its surroundings. A pot of boiling water is an open system because a burner supplies energy in the form of heat, and matter in the form of water vapor is lost as the water boils. A closed system can exchange energy but not matter with its surroundings. The sealed pouch of a ready-made dinner that is dropped into a pot of boiling water is a closed system because thermal energy is transferred to the system from the boiling water but no matter is exchanged (unless the pouch leaks, in which case it is no longer a closed system). An isolated system exchanges neither energy nor matter with the surroundings. Energy is always exchanged between a system and its surroundings, although this process may take place very slowly. A truly isolated system does not actually exist. An insulated thermos containing hot coffee approximates an isolated system, but eventually the coffee cools as heat is transferred to the surroundings. In all cases, the amount of heat lost by a system is equal to the amount of heat gained by its surroundings and vice versa. That is, *the total energy of a system plus its surroundings is constant*, which must be true if *energy is conserved*.

The state of a system is a complete description of a system at a given time, including its temperature and pressure, the amount of matter it contains, its chemical composition, and the physical state of the matter. A state function is a property of a system whose magnitude depends on only the present state of the system, not its previous history. Temperature, pressure, volume, and potential energy are all state functions. The temperature of an oven, for example, is independent of however many steps it may have taken for it to reach that temperature. Similarly, the pressure in a tire is independent of how often air is pumped into the tire for it to reach that pressure, as is the final volume of air in the tire. Heat and work, on the other hand, are not state functions because they are *path dependent*. For example, a car sitting on the top level of a parking garage has the same potential energy whether it was lifted by a crane, set there by a helicopter, driven up, or pushed up by a group of students (Figure 12.1.4). The amount of work expended to get it there, however, can differ greatly depending on the path chosen. If the students decided to carry the car to the top of the ramp, they would perform a great deal more work than if they simply pushed the car up the ramp (unless, of course, they neglected to release the parking brake, in which case the work expended would increase substantially!). The potential energy of the car is the same, however, no matter which path they choose.

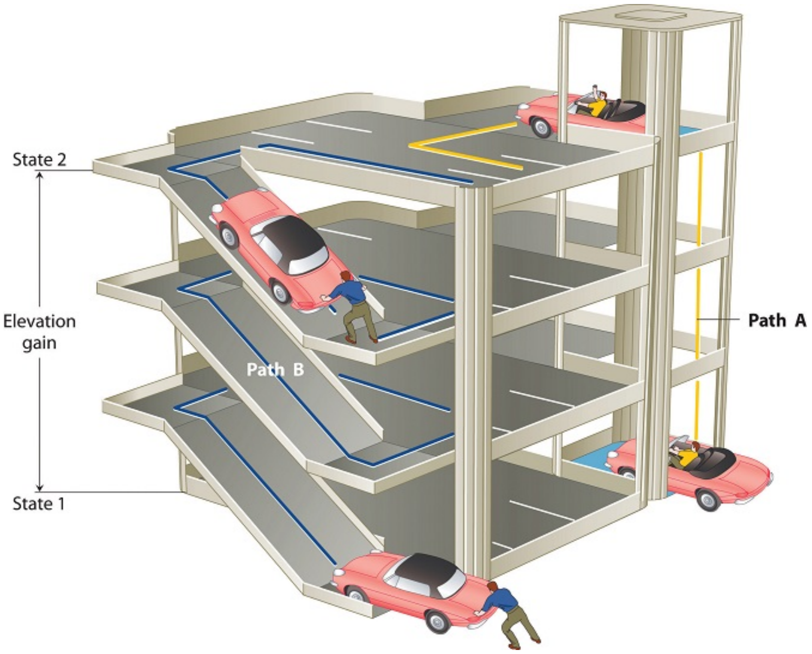


Figure 12.1.4: Elevation as an Example of a State Function. The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are *not* state functions. (CC BY-SA-NC; anonymous)

Summary

Thermochemistry is a branch of chemistry that qualitatively and quantitatively describes the energy changes that occur during chemical reactions. **Energy** is the capacity to do work. **Mechanical work** is the amount of energy required to move an object a given distance when opposed by a force. **Thermal energy** is due to the random motions of atoms, molecules, or ions in a substance. The **temperature** of an object is a measure of the amount of thermal energy it contains. **Heat (*q*)** is the transfer of thermal energy from a hotter object to a cooler one. Energy can take many forms; most are different varieties of **potential energy (*PE*)**, energy caused by the relative position or orientation of an object. **Kinetic energy (*KE*)** is the energy an object possesses due to its motion. Energy can be converted from one form to another, but the **law of conservation of energy** states that energy can be neither created nor destroyed. The most common units of energy are the **joule (J)**, defined as 1 $(kg \cdot m^2)/s^2$, and the **calorie**, defined as the amount of energy needed to raise the temperature of 1 g of water by 1°C (1 cal = 4.184 J).

12.2: The First Law of Thermodynamics - Internal Energy, Work, and Heat

Learning Objectives

- To calculate changes in internal energy
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

The relationship between the energy change of a system and that of its surroundings is given by the first law of thermodynamics, which states that the energy of the universe is constant. We can express this law mathematically as follows:

$$\Delta U_{univ} = \Delta U_{sys} + \Delta U_{surr} = 0 \tag{12.2.1}$$

or

$$\Delta U_{sys} = -\Delta U_{surr} \tag{12.2.2}$$

where the subscripts *univ*, *sys*, and *surr* refer to the universe, the system, and the surroundings, respectively. Thus the change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

> *The tendency of all systems, chemical or otherwise, is to move toward the state with the lowest possible energy.*

An important factor that determines the outcome of a chemical reaction is the tendency of all systems, chemical or otherwise, to move toward the lowest possible overall energy state. As a brick dropped from a rooftop falls, its potential energy is converted to kinetic energy; when it reaches ground level, it has achieved a state of lower potential energy. Anyone nearby will notice that energy is transferred to the surroundings as the noise of the impact reverberates and the dust rises when the brick hits the ground. Similarly, if a spark ignites a mixture of isooctane and oxygen in an internal combustion engine, carbon dioxide and water form spontaneously, while potential energy (in the form of the relative positions of atoms in the molecules) is released to the surroundings as heat and work. The internal energy content of the CO_2/H_2O product mixture is less than that of the isooctane O_2 reactant mixture. The two cases differ, however, in the form in which the energy is released to the surroundings. In the case of the falling brick, the energy is transferred as work done on whatever happens to be in the path of the brick; in the case of burning isooctane, the energy can be released as solely heat (if the reaction is carried out in an open container) or as a mixture of heat and work (if the reaction is carried out in the cylinder of an internal combustion engine). Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred (q) and the work done (w):

$$\underbrace{\Delta U_{sys} = q + w}_{\text{First Law of Thermodynamics}} \tag{12.2.3}$$

Although q and w are not state functions on their own, their sum (ΔU_{sys}) is independent of the path taken and is therefore a state function. A major task for the designers of any machine that converts energy to work is to maximize the amount of work obtained and minimize the amount of energy released to the environment as heat. An example is the combustion of coal to produce electricity. Although the maximum amount of energy available from the process is fixed by the energy content of the reactants and the products, the fraction of that energy that can be used to perform useful work is not fixed. Because we focus almost exclusively on the changes in the energy of a system, we will not use “sys” as a subscript unless we need to distinguish explicitly between a system and its surroundings.

> *Although q and w are not state functions, their sum (ΔU_{sys}) is independent of the path taken and therefore is a difference of a state function.*

Example 12.2.1

A sample of an ideal gas in the cylinder of an engine is compressed from 400 mL to 50.0 mL during the compression stroke against a constant pressure of 8.00 atm. At the same time, 140 J of energy is transferred from the gas to the surroundings as heat. What is the total change in the internal energy (ΔU) of the gas in joules?

Given: initial volume, final volume, external pressure, and quantity of energy transferred as heat

Asked for: total change in internal energy

Strategy:

A. Determine the sign of q to use in Equation 12.2.3.
B. From Equation 12.2.3 calculate w from the values given. Substitute this value into Equation 12.2.3 to calculate ΔU.

Solution

A From Equation 12.2.3, we know that $\Delta U = q + w$ (First Law of Thermodynamics). We are given the magnitude of q (140 J) and need only determine its sign. Because energy is transferred from the system (the gas) to the surroundings, q is negative by convention.

B Because the gas is being compressed, we know that work is being done on the system, so w must be positive. From Equation 12.2.3,

$$\begin{aligned} w &= -P_{\text{ext}} \Delta V \\ &= -8.00 \text{ atm}(0.0500 \text{ L} - 0.400 \text{ L}) \left(\frac{101.3 \text{ J}}{\text{L} \cdot \text{atm}} \right) \\ &= 284 \text{ J} \end{aligned}$$

Thus

$$\begin{aligned} \Delta U &= q + w \\ &= -140\ J + 284\ J \\ &= 144\ J \end{aligned}$$

In this case, although work is done on the gas, increasing its internal energy, heat flows from the system to the surroundings, decreasing its internal energy by 144 J. The work done and the heat transferred can have opposite signs.

Exercise 12.2.1

A sample of an ideal gas is allowed to expand from an initial volume of 0.200 L to a final volume of 3.50 L against a constant external pressure of 0.995 atm. At the same time, 117 J of heat is transferred from the surroundings to the gas. What is the total change in the internal energy (ΔU) of the gas in joules?

Answer

−216 J

By convention, both heat flow and work have a negative sign when energy is transferred from a system to its surroundings and vice versa.

Summary

The first law of thermodynamics states that the energy of the universe is constant. The change in the internal energy of a system is the sum of the heat transferred and the work done. The heat flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for ΔU.

12.3: Heat Capacity, Enthalpy, and Calorimetry

Learning Objectives

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data
- To use calorimetric data to calculate enthalpy changes.

Heat Capacity

We now introduce two concepts useful in describing heat flow and temperature change. The **heat capacity** (C) of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin)

$$C = \frac{q}{\Delta T} \tag{12.3.1}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an **extensive property**—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,140 J of energy to raise the temperature of the pan by 50.0 °C

$$C_{\text{small pan}} = \frac{18,140\ J}{50.0\ ^\circ C} = 363\ J/^\circ C$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

$$C_{\text{large pan}} = \frac{90,700\ J}{50.0\ ^\circ C} = 1814\ J/^\circ C$$

The *specific heat capacity* (c) of a substance, commonly called its **specific heat**, is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

$$c = \frac{q}{m\Delta T} \tag{12.3.2}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

$$c_{iron} = \frac{18,140\ J}{(808\ g)(50.0\ ^\circ C)} = 0.449\ J/g\ ^\circ C$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

$$c_{iron} = \frac{90,700 J}{(4,040\ g)(50.0\ ^\circ C)} = 0.449\ J/g\ ^\circ C$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure 12.3.1).

Figure 12.3.1: Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (CC BY; Mark Blaser via OpenStax).

The heat capacity of an object depends on both its *mass* and its *composition*. For example, doubling the mass of an object doubles its heat capacity. Consequently, the amount of substance must be indicated when the heat capacity of the substance is reported. The molar heat capacity (C_p) is the amount of energy needed to increase the temperature of 1 mol of a substance by 1°C; the units of C_p are thus J/(mol•°C).The subscript *p* indicates that the value was measured at constant pressure. The specific heat (c_s) is the amount of energy needed to increase the temperature of 1 g of a substance by 1°C; its units are thus J/(g•°C).

We can relate the quantity of a substance, the amount of heat transferred, its heat capacity, and the temperature change either via moles (Equation 12.3.3) or mass (Equation 12.3.4):

$$q = nc_p\Delta T \tag{12.3.3}$$

where

- n is the number of moles of substance and
- c_p is the *molar heat capacity* (i.e., heat capacity per **mole** of substance), and
- $\Delta T = T_{final} - T_{initial}$ is the temperature change.

$$q = mc_s\Delta T \tag{12.3.4}$$

where

- m is the mass of substance in grams,
- c_s is the *specific heat* (i.e., heat capacity per **gram** of substance), and
- $\Delta T = T_{final} - T_{initial}$ is the temperature change.

Both Equations 12.3.3 and 12.3.4 are under constant pressure (which matters) and both show that we know the amount of a substance and its specific heat (for mass) or molar heat capcity (for moles), we can determine the amount of heat, *q*, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost.

The specific heats of some common substances are given in Table 12.3.1. Note that the specific heat values of most solids are less than 1 J/(g•°C), whereas those of most liquids are about 2 J/(g•°C). Water in its solid and liquid states is an exception. The heat capacity of ice is twice as high as that of most solids; the heat capacity of liquid water, 4.184 J/(g•°C), is one of the highest known. The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table 12.3.1.

Table 12.3.1: Specific Heats of Common Substances at 25 °C and 1 bar

Substance	Symbol (state)	Specific Heat (J/g °C)
helium	He(*g*)	5.193
water	$H_2O(l)$	4.184
ethanol	$C_2H_6O(l)$	2.376
ice	$H_2O(s)$	2.093 (at −10 °C)
water vapor	$H_2O(g)$	1.864

Substance	Symbol (state)	Specific Heat (J/g °C)
nitrogen	$N_2(g)$	1.040
air	mixture	1.007
oxygen	$O_2(g)$	0.918
aluminum	$Al(s)$	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	$Ar(g)$	0.522
iron	$Fe(s)$	0.449
copper	$Cu(s)$	0.385
lead	$Pb(s)$	0.130
gold	$Au(s)$	0.129
silicon	$Si(s)$	0.712
quartz	$SiO_2(s)$	0.730

The value of C is intrinsically a positive number, but ΔT and q can be either positive or negative, and they both must have the same sign. If ΔT and q are positive, then *heat flows from the surroundings into an object*. If ΔT and q are negative, then *heat flows from an object into its surroundings.*

If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, then $\Delta T > 0$ and q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, so $\Delta T < 0$ and q is negative.

✓ Example 12.3.1: Measuring Heat

A flask containing $8.0 \times 10^2\ g$ of water is heated, and the temperature of the water increases from $21\ ^\circ C$ to $85\ ^\circ C$. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 800 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C (Table 12.3.1), so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need 800 times as much to heat 800 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need 64 times as much to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using Equation 12.3.4:

$$
\begin{aligned}
q &= mc_s\Delta T \\
&= mc_s(T_{\text{final}} - T_{\text{initial}}) \\
&= (4.184\ \text{J}/\cancel{\text{g}}\,^\circ\text{C}) \times (800\ \cancel{\text{g}}) \times (85-21)\,^\circ\text{C} \\
&= (4.184\ \text{J}/\cancel{\text{g}}\,^\circ\cancel{\text{C}}) \times (800\ \cancel{\text{g}}) \times (64)\,^\circ\cancel{\text{C}} \\
&= 210,000\ \text{J} (= 210\ \text{kJ})
\end{aligned}
$$

Because the temperature increased, the water absorbed heat and q is positive.

? Exercise 12.3.1

How much heat, in joules, must be added to a $5.00 \times 10^2\ g$ iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.451 J/g °C.

Answer

$5.07 \times 10^4\ J$

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

✓ Example 12.3.2: Determining Other Quantities

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C. Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using Equation 12.3.4:

$$q = mc_s \Delta T \qquad = mc_s (T_{final} - T_{initial})$$

Substituting the known values:

$$6,640\ J = (348\ g)c_s(43.6 - 22.4)\ ^\circ C$$

Solving:

$$c = \frac{6,640\ J}{(348\ g)(21.2^\circ C)} = 0.900\ J/g\ ^\circ C$$

Comparing this value with the values in Table $12.3.1$, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

? Exercise 12.3.2

A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C. Determine the specific heat of this metal, and predict its identity.

Answer

$c = 0.45\ J/g\ ^\circ C$; the metal is likely to be iron from checking Table $12.3.1$

✓ Example 12.3.3: Solar Heating

A home solar energy storage unit uses 400 L of water for storing thermal energy. On a sunny day, the initial temperature of the water is 22.0°C. During the course of the day, the temperature of the water rises to 38.0°C as it circulates through the water wall. How much energy has been stored in the water? (The density of water at 22.0°C is 0.998 g/mL.)

Passive solar system. During the day (a), sunlight is absorbed by water circulating in the water wall. At night (b), heat stored in the water wall continues to warm the air inside the house.

Given: volume and density of water and initial and final temperatures

Asked for: amount of energy stored

Strategy:

A. Use the density of water at 22.0°C to obtain the mass of water (m) that corresponds to 400 L of water. Then compute ΔT for the water.
B. Determine the amount of heat absorbed by substituting values for m, c_s, and ΔT into Equation 12.3.1.

Solution:

A The mass of water is

$$mass\ of\ H_2O = 400\ \cancel{L} \left(\frac{1000\ m\cancel{L}}{1\ \cancel{L}}\right)\left(\frac{0.998\ g}{1\ m\cancel{L}}\right) = 3.99 \times 10^5 g\ H_2O$$

The temperature change (ΔT) is 38.0°C − 22.0°C = +16.0°C.

B From Table 12.3.1, the specific heat of water is 4.184 J/(g•°C). From Equation 12.3.4, the heat absorbed by the water is thus

$$q = mc_s\Delta T = \left(3.99 \times 10^5\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g} \cdot \cancel{{}^\circ C}}\right)\left(16.0\ \cancel{{}^\circ C}\right) = 2.67 \times 10^7 J = 2.67 \times 10^4 kJ$$

Both q and ΔT are positive, consistent with the fact that the water has absorbed energy.

? Exercise 12.3.3: Solar Heating

Some solar energy devices used in homes circulate air over a bed of rocks that absorb thermal energy from the sun. If a house uses a solar heating system that contains 2500 kg of sandstone rocks, what amount of energy is stored if the temperature of the rocks increases from 20.0°C to 34.5°C during the day? Assume that the specific heat of sandstone is the same as that of quartz (SiO_2) in Table 12.3.1.

Answer

$2.7 \times 10^4\ kJ$

Even though the mass of sandstone is more than six times the mass of the water in Example 12.3.1, the amount of thermal energy stored is the same to two significant figures.

Heat "Flow" to Thermal Equilibrium

When two objects at different temperatures are placed in contact, heat flows from the warmer object to the cooler one until the temperature of both objects is the same. The law of conservation of energy says that the total energy cannot change during this process:

$$q_{cold} + q_{hot} = 0 \tag{12.3.5}$$

The equation implies that the amount of heat that flows *from* a warmer object is the same as the amount of heat that flows *into* a cooler object. Because the direction of heat flow is opposite for the two objects, the sign of the heat flow values must be opposite:

$$q_{cold} = -q_{hot} \tag{12.3.6}$$

Thus heat is conserved in any such process, consistent with the law of conservation of energy.

> *The amount of heat lost by a warmer object equals the amount of heat gained by a cooler object.*

Substituting for q from Equation 12.3.4 gives

$$[mc_s \Delta T]_{cold} + [mc_s \Delta T]_{hot} = 0$$

which can be rearranged to give

$$[mc_s \Delta T]_{cold} = -[mc_s \Delta T]_{hot} \tag{12.3.7}$$

When two objects initially at different temperatures are placed in contact, we can use Equation 12.3.7 to calculate the final temperature if we know the chemical composition and mass of the objects.

✓ Example 12.3.4: Thermal Equilibration of Copper and Water

If a 30.0 g piece of copper pipe at 80.0°C is placed in 100.0 g of water at 27.0°C, what is the final temperature? Assume that no heat is transferred to the surroundings.

Given: mass and initial temperature of two objects

Asked for: final temperature

Strategy: Using Equation 12.3.7 and writing $\Delta T = T_{final} - T_{initial}$ for both the copper and the water, substitute the appropriate values of m, c_s, and $T_{initial}$ into the equation and solve for T_{final}.

Solution

We can adapt Equation 12.3.7 to solve this problem, remembering that $\Delta T = T_{final} - T_{initial}$:

$$[mc_s \left(T_{final} - T_{initial}\right)]_{Cu} + [mc_s \left(T_{final} - T_{initial}\right)]_{H_2O} = 0$$

Substituting the data provided in the problem and Table 12.3.1 gives

$$\begin{aligned} (30\ g)\,(0.385\ J/(g^{\circ}C))(T_{final} - 80^{\circ}C) + (100\ g)(4.184\ J/(g^{\circ}C))(T_{final} - 27.0^{\circ}C) &= 0 \\ T_{final}\,(11.6\ J/^{o}C) - 924\ J + T_{final}\,(418.4\ J/^{o}C) - 11,300\ J &= 0 \\ T_{final}\,(430\ J/\ (g \cdot^{o} C)) &= 12,224\ J \\ T_{final} &= 28.4\ ^{o}C \end{aligned}$$

? Exercise 12.3.4A: Thermal Equilibration of Gold and Water

If a 14.0 g chunk of gold at 20.0°C is dropped into 25.0 g of water at 80.0°C, what is the final temperature if no heat is transferred to the surroundings?

Answer

80.0°C

? Exercise 12.3.4B: Thermal Equilibration of Aluminum and Water

A 28.0 g chunk of aluminum is dropped into 100.0 g of water with an initial temperature of 20.0°C. If the final temperature of the water is 24.0°C, what was the initial temperature of the aluminum? (Assume that no heat is transferred to the surroundings.)

Answer

90.6°C

Measuring Heat "Flow"

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The change in temperature of the measuring part of the calorimeter is converted into the amount of heat (since the previous calibration was used to establish its heat capacity). The measurement of heat transfer using this approach requires the definition of a system (the substance or substances undergoing the chemical or physical change) and its surroundings (the other components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system). Knowledge of the heat capacity of the surroundings, and careful measurements of the masses of the system and surroundings and their temperatures before and after the process allows one to calculate the heat transferred as described in this section.

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process.

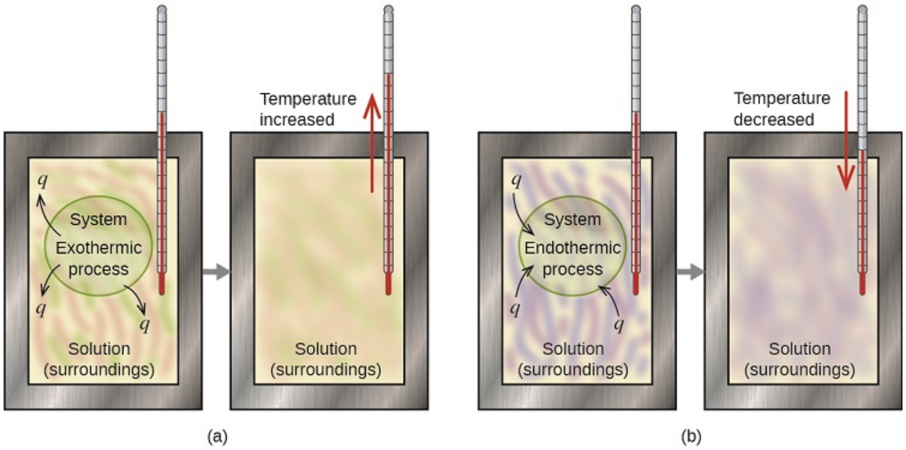


Figure 12.3.2: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system.

The thermal energy change accompanying a chemical reaction is responsible for the change in temperature that takes place in a calorimeter. If the reaction releases heat ($q_{\text{rxn}} < 0$), then heat is absorbed by the calorimeter ($q_{\text{calorimeter}} > 0$) and its temperature increases. Conversely, if the reaction absorbs heat ($q_{\text{rxn}} > 0$), then heat is transferred from the calorimeter to the system ($q_{\text{calorimeter}} < 0$) and the temperature of the calorimeter decreases. In both cases, *the amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction*. The heat capacity of the calorimeter or of the reaction mixture may be used to calculate the amount of heat released or absorbed by the chemical reaction. The amount of heat released or absorbed per gram or mole of reactant can then be calculated from the mass of the reactants.

> *The amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction.*

Constant-Pressure Calorimetry

Because ΔH is defined as the heat flow at constant pressure, measurements made using a constant-pressure calorimeter (a device used to measure enthalpy changes in chemical processes at constant pressure) give ΔH values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. A “student” version, called a *coffee-cup* *calorimeter* (Figure 12.3.3), is often encountered in general chemistry laboratories. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as several millionths of a degree (10^{-6} °C).

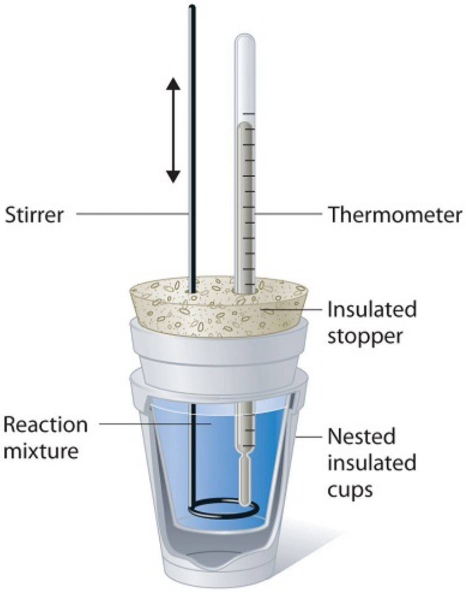


Figure 12.3.3: A Coffee-Cup Calorimeter. This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.

Before we practice calorimetry problems involving chemical reactions, consider a simpler example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium. If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter's surroundings. Under these ideal circumstances, the net heat change is zero:

$$q_{\text{substance M}} + q_{\text{substance W}} = 0 \tag{12.3.8}$$

This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

$$q_{\text{substance M}} = -q_{\text{substance W}} \tag{12.3.9}$$

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that $q_{substance\ M}$ and $q_{substance\ W}$ are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either q value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described, $q_{substance\ M}$ is a negative value and $q_{\text{substance W}}$ is positive, since heat is transferred from M to W.

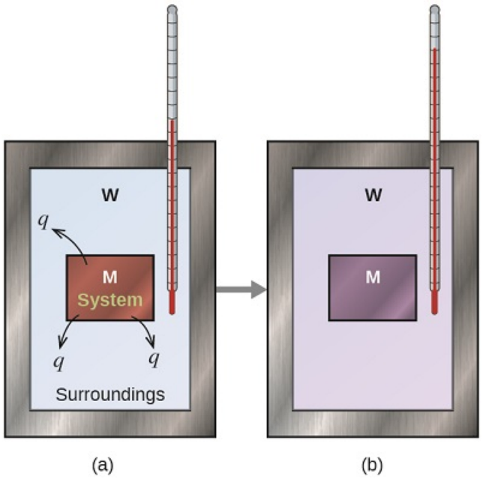


Figure 12.3.4: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

✓ Example 12.3.5: Heat between Substances at Different Temperatures

A 360-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water was measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table T4), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat “lost” to the surroundings, then heat given off by rebar = −heat taken in by water, or:

$$q_{\text{rebar}} = -q_{\text{water}}$$

Since we know how heat is related to other measurable quantities, we have:

$$(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}}$$

Letting f = final and i = initial, in expanded form, this becomes:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{\text{f,rebar}} - T_{\text{i,rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

$$(0.449\ \text{J/g}\ ^\circ\text{C})(360\text{g})(42.7^\circ\text{C} - T_{\text{i,rebar}}) = -(4.184\ \text{J/g}\ ^\circ\text{C})(425\ \text{g})(42.7^\circ\text{C} - 24.0^\circ\text{C})$$

$$T_{\text{i,rebar}} = \frac{(4.184\ \text{J/g}\ ^\circ\text{C})(425\ \text{g})(42.7^\circ\text{C} - 24.0^\circ\text{C})}{(0.449\ \text{J/g}\ ^\circ\text{C})(360\ \text{g})} + 42.7^\circ\text{C}$$

Solving this gives $T_{i,rebar}$ = 248 °C, so the initial temperature of the rebar was 248 °C.

? Exercise 12.3.5A

A 248-g piece of copper is dropped into 390 mL of water at 22.6 °C. The final temperature of the water was measured as 39.9 °C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

Answer

The initial temperature of the copper was 335.6 °C.

Exercise 12.3.5B

A 248-g piece of copper initially at 314 °C is dropped into 390 mL of water initially at 22.6 °C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

Answer

The final temperature (reached by both copper and water) is 38.8 °C.

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

✓ Example 12.3.6: Identifying a Metal by Measuring Specific Heat

A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0 °C. The final temperature is 28.5 °C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.

Solution

Assuming perfect heat transfer, heat given off by metal = −heat taken in by water, or:

$$q_{\text{metal}} = -q_{\text{water}}$$

In expanded form, this is:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{\text{f,metal}} - T_{\text{i,metal}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0 °C; and that for water, 60.0 mL = 60.0 g; we have:

$$(c_{\text{metal}})(59.7\text{ g})(28.5^\circ\text{C} - 100.0^\circ\text{C}) = -(4.18\text{ J/g }^\circ\text{C})(60.0\text{ g})(28.5^\circ\text{C} - 22.0^\circ\text{C})$$

Solving this:

$$c_{\text{metal}} = \frac{-(4.184\text{ J/g }^\circ\text{C})(60.0\text{ g})(6.5^\circ\text{C})}{(59.7\text{ g})(-71.5^\circ\text{C})} = 0.38\text{ J/g }^\circ\text{C}$$

Comparing this with values in Table T4, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

Exercise 12.3.6

A 92.9-g piece of a silver/gray metal is heated to 178.0 °C, and then quickly transferred into 75.0 mL of water initially at 24.0 °C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7 °C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

Answer

$$c_{metal} = 0.13\ J/g\ ^\circ C$$

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the surroundings. Because energy is neither created nor destroyed during a chemical reaction, there is no overall energy change during the reaction. The heat produced or consumed in the reaction (the “system”), q_{reaction}, plus the heat absorbed or lost by the solution (the “surroundings”), q_{solution}, must add up to zero:

$$q_{\text{reaction}} + q_{\text{solution}} = 0 \tag{12.3.10}$$

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

$$q_{\text{reaction}} = -q_{\text{solution}} \tag{12.3.11}$$

This concept lies at the heart of all calorimetry problems and calculations. Because the heat released or absorbed at constant pressure is equal to ΔH, the relationship between heat and ΔH_{rxn} is

$$\Delta H_{rxn} = q_{rxn} = -q_{calorimater} = -mc_s\Delta T \tag{12.3.12}$$

The use of a constant-pressure calorimeter is illustrated in Example 12.3.7.

✓ Example 12.3.7: Heat of Solution

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0°C to 34.7°C. The density of water in this temperature range averages 0.9969 g/cm^3. What is ΔH_{soln} (in kilojoules per mole)? Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

Given: mass of substance, volume of solvent, and initial and final temperatures

Asked for: ΔH_{soln}

Strategy:

A. Calculate the mass of the solution from its volume and density and calculate the temperature change of the solution.
B. Find the heat flow that accompanies the dissolution reaction by substituting the appropriate values into Equation 12.3.1.
C. Use the molar mass of KOH to calculate ΔH_{soln}.

Solution:

A To calculate ΔH_{soln}, we must first determine the amount of heat released in the calorimetry experiment. The mass of the solution is

$$\left(100.0\ \cancel{mL}\ \mathrm{H_2O}\right)\left(0.9969\ g/\ \cancel{mL}\right) + 5.03\ g\ KOH = 104.72\ g$$

The temperature change is (34.7°C − 23.0°C) = +11.7°C.

B Because the solution is not very concentrated (approximately 0.9 M), we assume that the specific heat of the solution is the same as that of water. The heat flow that accompanies dissolution is thus

$$\begin{aligned} q_{calorimater} &= mc_s\Delta T \\ &= \left(104.72\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot \cancel{^\circ C}}\right)\left(11.7\ \cancel{^\circ C}\right) \\ &= 5130\ J \\ &= 5.13\ kJ \end{aligned}$$

The temperature of the solution increased because heat was absorbed by the solution ($q > 0$). Where did this heat come from? It was released by KOH dissolving in water. From Equation 12.3.1, we see that

$$\Delta H_{rxn} = -q_{calorimeter} = -5.13\ kJ$$

This experiment tells us that dissolving 5.03 g of KOH in water is accompanied by the *release* of 5.13 kJ of energy. Because the temperature of the solution increased, the dissolution of KOH in water must be exothermic.

C The last step is to use the molar mass of KOH to calculate ΔH_{soln} - the heat associated when dissolving 1 mol of KOH:

$$\begin{aligned}\Delta H_{soln} &= \left(\frac{5.13\ kJ}{5.03\ \cancel{g}}\right)\left(\frac{56.11\ \cancel{g}}{1\ mol}\right) \\ &= -57.2\ kJ/mol\end{aligned}$$

? Exercise 12.3.7: Heat of Dissolving

A coffee-cup calorimeter contains 50.0 mL of distilled water at 22.7°C. Solid ammonium bromide (3.14 g) is added and the solution is stirred, giving a final temperature of 20.3°C. Using the same assumptions as in Example 12.3.7, find ΔH_{soln} for NH_4Br (in kilojoules per mole).

Answer

16.6 kJ/mol

Constant-Volume Calorimetry

Constant-pressure calorimeters are not very well suited for studying reactions in which one or more of the reactants is a gas, such as a combustion reaction. The enthalpy changes that accompany combustion reactions are therefore measured using a constant-volume calorimeter, such as the bomb calorimeter (A device used to measure energy changes in chemical processes. shown schematically in Figure 12.3.4). The reactant is placed in a steel cup inside a steel vessel with a fixed volume (the “bomb”). The bomb is then sealed, filled with excess oxygen gas, and placed inside an insulated container that holds a known amount of water. Because combustion reactions are exothermic, the temperature of the bath and the calorimeter increases during combustion. If the heat capacity of the bomb and the mass of water are known, the heat released can be calculated.

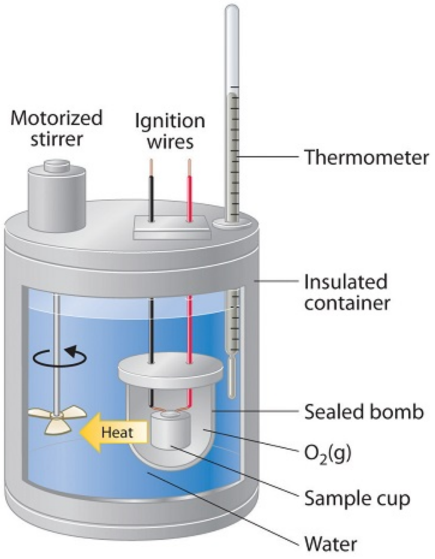


Figure 12.3.4: A Bomb Calorimeter. After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction. (CC BY-SA-NC; anonymous)

Because the volume of the system (the inside of the bomb) is fixed, the combustion reaction occurs under conditions in which the volume, but not the pressure, is constant. The heat released by a reaction carried out at constant volume is identical to the change in *internal energy* (ΔU) rather than the enthalpy change (ΔH); ΔU is related to ΔH by an expression that depends on the change in the number of moles of gas during the reaction. The difference between the heat flow measured at constant volume and the enthalpy change is usually quite small, however (on the order of a few percent). Assuming that $\Delta U < \Delta H$, the relationship between the measured temperature change and ΔH_{comb} is given in Equation 12.3.13, where C_{bomb} is the total heat capacity of the steel bomb and the water surrounding it

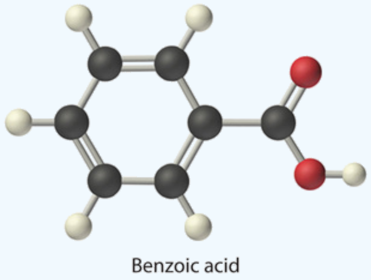
$$\Delta H_{comb} < q_{comb} = q_{calorimater} = C_{bomb}\Delta T \tag{12.3.13}$$

To measure the heat capacity of the calorimeter, we first burn a carefully weighed mass of a standard compound whose enthalpy of combustion is accurately known. Benzoic acid ($C_6H_5CO_2H$) is often used for this purpose because it is a crystalline solid that can be obtained in high purity. The combustion of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat per gram (i.e., its ΔH_{comb} = −26.38 kJ/g). This value and the measured increase in temperature of the calorimeter can be used to determine C_{bomb}. The use of a bomb calorimeter to measure the ΔH_{comb} of a substance is illustrated in Example $12.3.8$

Video $\mathbf{12.3.1}$***:*** *Video of view how a bomb calorimeter is prepared for action.*

✓ Example 12.3.8: Combustion of Glucose

The combustion of 0.579 g of benzoic acid in a bomb calorimeter caused a 2.08°C increase in the temperature of the calorimeter. The chamber was then emptied and recharged with 1.732 g of glucose and excess oxygen. Ignition of the glucose resulted in a temperature increase of 3.64°C. What is the ΔH_{comb} of glucose?



Given: mass and ΔT for combustion of standard and sample

Asked for: ΔH_{comb} of glucose

Strategy:

A. Calculate the value of q_{rxn} for benzoic acid by multiplying the mass of benzoic acid by its ΔH_{comb}. Then use Equation 12.3.1 to determine the heat capacity of the calorimeter (C_{bomb}) from q_{comb} and ΔT.
B. Calculate the amount of heat released during the combustion of glucose by multiplying the heat capacity of the bomb by the temperature change. Determine the ΔH_{comb} of glucose by multiplying the amount of heat released per gram by the molar mass of glucose.

Solution:

The first step is to use Equation 12.3.1 and the information obtained from the combustion of benzoic acid to calculate C_{bomb}. We are given ΔT, and we can calculate q_{comb} from the mass of benzoic acid:

$$q_{comb} = \left(0.579\ \cancel{g}\right)\left(-26.38\ kJ/\ \cancel{g}\right) = -15.3\ kJ$$

From Equation 12.3.1,

$$-C_{bomb} = \frac{q_{comb}}{\Delta T} = \frac{-15.3\ kJ}{2.08\ ^{o}C} = -7.34\ kJ/^{o}C$$

B According to the strategy, we can now use the heat capacity of the bomb to calculate the amount of heat released during the combustion of glucose:

$$q_{comb} = -C_{bomb}\Delta T = (-7.34\ kJ/^{o}C)\,(3.64\ ^{o}C) = -26.7\ kJ$$

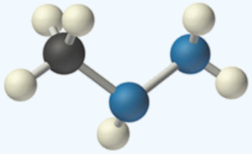
Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the ΔH_{comb} of glucose is

$$\Delta H_{comb} = \left(\frac{-26.7\ kJ}{1.732\ \cancel{g}}\right)\left(\frac{180.16\ \cancel{g}}{mol}\right) = -2780\ kJ/mol = 2.78 \times 10^{3}\ kJ/mol$$

This result is in good agreement (< 1% error) with the value of $\Delta H_{comb} = -2803\ kJ/mol$ that calculated using enthalpies of formation.

? Exercise 12.3.8: Combustion of Benzoic Acid

When 2.123 g of benzoic acid is ignited in a bomb calorimeter, a temperature increase of 4.75°C is observed. When 1.932 g of methylhydrazine (CH_3NHNH_2) is ignited in the same calorimeter, the temperature increase is 4.64°C. Calculate the ΔH_{comb} of methylhydrazine, the fuel used in the maneuvering jets of the US space shuttle.



Methylhydrazine

Answer

-1.30×10^3 kJ/mol

Summary

Calorimetry measures enthalpy changes during chemical processes, where the magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. **Calorimetry** is the set of techniques used to measure enthalpy changes during chemical processes. It uses devices called *calorimeters*, which measure the change in temperature when a chemical reaction is carried out. The magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. The **heat capacity (*C*)** of an object is the amount of energy needed to raise its temperature by 1°C; its units are joules per degree Celsius. The **specific heat** (c_s) of a substance is the amount of energy needed to raise the temperature of 1 g of the substance by 1°C, and the **molar heat capacity** (c_p) is the amount of energy needed to raise the temperature of 1 mol of a substance by 1°C. Liquid water has one of the highest specific heats known. Heat flow measurements can be made with either a **constant-pressure calorimeter**, which gives ΔH values directly, or a **bomb calorimeter**, which operates at constant volume and is particularly useful for measuring enthalpies of combustion.

Thermal energy itself cannot be measured easily, but the temperature change caused by the flow of thermal energy between objects or substances can be measured. Calorimetry describes a set of techniques employed to measure enthalpy changes in chemical processes using devices called *calorimeters*. To have any meaning, the quantity that is actually measured in a calorimetric experiment, the change in the temperature of the device, must be related to the heat evolved or consumed in a chemical reaction. We begin this section by explaining how the flow of thermal energy affects the temperature of an object.

Contributors and Attributions

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12.4: Illustrations of the First Law of Thermodynamics in Ideal Gas Processes

12.5: Thermochemistry

12.6: Reversible Processes in Ideal Gases

12.E: Thermodynamic Processes (Exercises)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

Q1A

A sample of O_2 gas is under an external pressure of 17 atm and contained in a cylinder with a volume of 50 L. The gas is cooled and the resulting volume is 25 L. Calculate the amount of work done **on** the O_2 gas.

Solution

$$\begin{aligned} w &= -P\Delta V \\ &= -P_{\text{ext}}(V_2 - V_1) \\ &= -17 atm\ (25\ L - 50\ L) = 425\ L\ atm \\ &= 425\ atm\ L\ (101.325 \frac{J}{atm\ L}) \\ &= 43,063\ J \\ &= 43.06\ kJ \end{aligned}$$

Q1B

A system containing oxygen gas is heated at a constant pressure of 40.0 atm so that its volume increases 177 L to 458 L. Express the amount of work that the system did in kilo-joules.

Solution

The formula for work from the expansion of a gas at constant pressure

$$w = -P_{ext}\Delta V$$

$$w = -40\ atm \times (458\ L - 177\ L) = -11240\ L\ atm$$

Convert from L atm to joules

$$-11240\ L\ atm \times 101.325\ \frac{J}{L\ atm} = -1138893\ J$$

Convert from J to kJ and round to get the final answer

$$-1138893\ J \times \frac{1\ kJ}{1000\ J} = -1140\ kJ$$

$$w = -1140\ kJ$$

Q2

The gas mixture inside one of the cylinders of an airplane expands against a constant external pressure of 5.00 atm because of the growing altitude, from an initial volume of 500 mL (at the end of the compression stroke) to the final volume of 1200 mL. Calculate the work done on the gas mixture during this process and express it in Joules.

Solution

$$w = -(5.00\text{ atm})(1200\text{ mL} - 500\text{ mL})(\frac{1\text{ L}}{1000\text{ mL}})(101.3\ \frac{\text{J}}{\text{L}\times\text{atm}}) = -354.55\text{ J}$$

Q3

The following events are based on a true story. A butcher for the local Chinese restaurant needs to defrost a large chunk of beef, which weights 50 lb and is currently at $0^\circ C$. He wants to accomplish this by is going out onto the street and repeatedly drop it onto the ground. Suppose the potential energy of the meat completely transforms into heat each time it hits the ground, and that energy can be calculated from

$$V = mg\Delta h$$

where m is mass of the object, g is the acceleration of gravity, and Δh is change in height. If the man is $5\,\text{ft}$ tall and he wants to get the meat to room temperature (25°C), how many times does he have to drop the piece of meat? Assume the environment has no effect on the meat, and that it does not lose any heat. (Specific Heat of the Meat: $0.25\,\frac{\text{J}}{\text{g}^\circ\text{C}}$).

Solution

There are two steps to solve this equation. First, to find the amount of heat absorbed by the meat from one drop. Second, to find the total amount of heat needed to warm the meat up from $0^{\circ}C$ to $25^{\circ}C$.

To find the total amount of heat required to bring the meat from $0^{\circ}C$ to $25^{\circ}C$, the equation for calculating heat has to be used:

$$Q = mC_p\Delta T$$

The mass of the meat can be calculated via conversion from lb to g, and is as follows:

$$50lb \times 453.592\frac{g}{lb} = 22679.6g$$

The change in temperature is just the final temperature minus the initial, so it is just $25^{\circ}C$.

Lastly, C_p is given. Plugging in all of these values gives:

$$Q = 22679.6g \times 0.25\frac{J}{g^{\circ}C} \times 25^{\circ}C = 141747.5J$$

Thus, $141747.5J$ is the total amount of heat needed to heat up the meat to $25^{\circ}C$.

Now to find the amount of heat transferred into the meat from one drop. This utilizes the potential energy equation. The question mentions how to calculate the potential energy, and all potential energy is translated into heat. Therefore.

$$Q = V = mg\Delta h$$

The problem gives the mass, the acceleration of gravity is $9.8\frac{m}{s^2}$, and height. Therefore, since the potential energy for one drop is equal to the heat for one drop, the heat can be calculated as such:

$$Q = 22.6796kg \times 9.8\frac{m}{s^2} \times 1.524m = 338.724\frac{kg\,m^2}{s^2} = 338.724J$$

From there, since no heat is lost, it carries over for each drop. Therefore, the number of times he needs to drop the meat is found by simple division:

$$141747.5J \div 338.724J = 418.474drops$$

Thus, the drops needed is around 419.

Abstract: Calculate heat from $Q = mC_p\Delta T$ and $Q = V = mg\Delta h$. Divide the two.

Q4

Suppose you have a ball ($C_p = 0.85\frac{J}{g^oC}$) at 25°C, what will its final temperature be if the amount of work equal to dropping it down from a height of 86.6m is done to it ? ($g = 9.81\frac{m}{s^2}$)

Solution

$$\begin{aligned} U &= mg\Delta h \quad (12.E.1)\\ &= m_{ball} \cdot 86.6m \cdot 9.81\frac{m}{s^2} \quad (12.E.2)\\ &= 850m_{ball} \quad (12.E.3)\end{aligned}$$

If we assuming all the kinetic energy at the time of collision converts to heat, then

$$\begin{aligned} \Delta T &= \frac{q}{Cp \cdot m_{ball}} \quad (12.E.4)\\ &= \frac{U}{C_p \cdot m_{ball}} \quad (12.E.5)\\ &= \frac{850m_{ball}}{85\frac{J}{g^oC} \cdot m_{ball}}\frac{1\,kg}{1,000\,g} \quad (12.E.6)\\ &= 1.0^{\circ}C \quad (12.E.7)\\ T_{final} &= 25^{\circ}C + 1^{\circ}C \quad (12.E.8)\\ &= 26^{\circ}C \quad (12.E.9)\end{aligned}$$

Q7A

The rule of Dulong and Petit shows that the molar heat capacities of most metallic elements group around a certain value “X” $\frac{J}{K\,mol}$ at 25^{o}C. By first calculating and showing the molar heat capacities of metals rhenium, silver, lead, tungsten, copper, molybdenum and hafnium (given that the respective specific heat capacities of these metals are $0.14\frac{J}{K\,g}$, $0.23\frac{J}{K\,g}$, $0.13\frac{J}{K\,g}$, $0.13\frac{J}{K\,g}$, $0.39\frac{J}{K\,g}$, $0.25\frac{J}{K\,g}$ and $0.14\frac{J}{K\,g}$), find the value of “X”. (hint: take the average value of the calculated molar heat capacities and round off value to nearest whole number).

Solution

To first find the molar heat capacities of each metal, multiply the molar mass of each metal by their specific heat capacities:

Molar heat capacity of:

$$\mathrm{Re} = 0.14\frac{J}{K\,g}\times 186.207\frac{g}{mol} = 26.068\frac{J}{K\,mol}\mathrm{Ag} = 0.23\frac{J}{K\,g}\times 107.868\frac{g}{mol} = 24.809\frac{J}{K\,mol}$$

$$\mathrm{Pb} = 0.13\frac{J}{K\,g}\times 207.2\frac{g}{mol} = 26.936\frac{J}{K\,mol}$$

calculate the average molar heat capacity:

Average molar heat capacity= $\frac{1}{7}(26.068\frac{J}{K\,mol} + 24.809\frac{J}{K\,mol} + 26.936\frac{J}{K\,mol} + 23.899\frac{J}{K\,mol} + 24.7829\frac{J}{K\,mol} + 23.99\frac{J}{K\,mol} + 24.988\frac{J}{K\,mol}) = 25.068\frac{J}{K\,mol}$

$$\mathrm{W} = 0.13\frac{J}{K\,g}\times 183.84\frac{g}{mol} = 23.899\frac{J}{K\,mol}$$

$$\mathrm{Cu} = 0.39\frac{J}{K\,g}\times 63.546\frac{g}{mol} = 24.7829\frac{J}{K\,mol}$$

$$\mathrm{Mo} = 0.25\frac{J}{K\,g}\times 95.96\frac{g}{mol} = 23.99\frac{J}{K\,mol}$$

$$\mathrm{Hf} = 0.14\frac{J}{K\,g}\times 178.49\frac{g}{mol} = 24.988\frac{J}{K\,mol}$$

Q7B

The specific heat capacities of metals aluminum, bismuth, copper, lead, and silver at 25°C are 0.900, 0.123, 0.386, 0.128, and $0.233\frac{J}{g\,K}$. Calculate the molar heat capacities of these metals. According to the rule of Dulong and Petit, the molar heat capacities of metallic elements, like these, are approximately $25\frac{J}{K\,mol}$.

Solution

Multiply each of the specific heat capacities by its corresponding molar mass to obtain their molar heat capacities.

Aluminum:

$$0.900\frac{J}{g\,K}\times 26.98\frac{g}{mol} = 24.3\frac{J}{mol\,K}$$

Bismuth:

$$0.123\frac{J}{g\,K}\times 208.98\frac{g}{mol} = 25.7\frac{J}{mol\,K}$$

Copper:

$$0.386\frac{J}{g\,K}\times 63.55\frac{g}{mol} = 24.5\frac{J}{mol\,K}$$

Lead:

$$0.128\frac{J}{g\,K}\times 207.2\frac{g}{mol} = 26.5\frac{J}{mol\,K}$$

Silver:

$$0.223\frac{J}{g\,K}\times 107.87\frac{g}{mol} = 25.1\frac{J}{mol\,K}$$

Q9

An undisclosed volume of water is tightly sealed in a microwave-safe container at room temperature before it is placed in an ice bath where it is cooled by a student.

a. During the cooling process within the ice bath, state whether (ΔU), Q, and W of the system are negative, zero, or positive. Explain your reasoning.

b. After being cooled, the student decides that the water seems too cold so it is placed in the microwave where the container of water is heated back to room temperature. What are the new signs of (ΔU), Q, and W during the heating process? Explain your reasoning.
c. Now determine the signs of ($\Delta U_1 + \Delta U_2$), ($Q_1 + Q_2$) , and ($W_1 + W_2$), where possible, assuming that the cooling process was step 1 and the heating process was step 2.

Solution

a. *W* is *zero*, *Q* is *negative*, and (ΔU) is *negative*. Work is zero for this step because neither volume nor pressure of the container is changing. Since the water is cooler than before heat has left the system so it is negative; and because (ΔU) = Q + W and W = 0 then (ΔU) = Q which is negative so, (ΔU) is negative.
b. *W* is *zero*, *Q* is *positive*, and (ΔU) is *positive*. Work is zero for this step because neither volume nor pressure of the container is changing. Since the water is hotter than before heat has entered the system so it is positive and because (ΔU) = Q + W and W = 0 then (ΔU) = Q which is positive so, (ΔU) is positive.
c. Since *W* was equal to zero for both processes above (W_1 + W_2) is equal to *zero*. ($(\Delta U)_1$ + $(\Delta U)_2$) = (Q_1 + Q_2) where they are both equal to *zero*.

If the water is cooled from room temperature to a lower temperature and then heated directly back to room temperature, wouldn't ($(\Delta U)_1$ + $(\Delta U)_2$) be 0? Q is the only factor actually changing here and q(heating to cooling) = -q(cooling to heating) provided the change in t is the same. So both ($(\Delta U)_1$ + $(\Delta U)_2$) and q should be 0.

Q11A

Your lab partner slipped a sample of unknown hot metal that is 40.0g, which is initially at 130.0°C into a 100.0 g water that is initially at 50.0°C. A temperature probe indicates that equilibrium is reached at 60.15°C. Using the specific heat capacity of water $4.18 \frac{J}{K}$, calculate the specific heat capacity of the unknown metal.

Solution

Imagine two sub-systems: the metal and the water. If mixing the hot metal and cool water inside a well-insulated container (that prevent leaks of heat), then the heat absorbed by the system will equal zero. Since the system is the sum of the two sub-systems:

$$q_{\text{sys}} = 0 = q_{\text{metal}} + q_{\text{water}}$$

For both sub-systems, the amount of heat gained is equal to the specific heat capacity times the mass times the temperature change:

$$q_{\text{metal}} + q_{\text{water}} = m_{\text{water}} C_{s,\text{water}}\ \Delta T_{\text{metal}} = 0$$

Solving for the specific heat capacity of the metal:

$$c_{s,\text{metal}} = \frac{-m_{\text{water}} c_{s,\text{water}}\ \Delta T_{\text{water}}}{m_{\text{metal}} \Delta T_{\text{metal}}} = \frac{-100.0\text{ g} \times 4.18 \dfrac{\text{J}}{\text{K g}} \times 10.15^\circ\text{C}}{40.0\text{ g} \times -69.85^\circ\text{C}} = 1.52 \frac{\text{J}}{\text{K g}}$$

Tip: Do not convert Celsius to Kelvin. The Kelvin and Celsius scales differ only in their location of their zero points. Temperature change in Celsius is the same temperature change of Kelvin.

Q11B

Let's say you 34.5 grams of some hot metal that is initially at 75°C and you put that metal into 64.0 grams of water that is initially at 25°C. If the the two objects reach thermal equilibrium at 39°C, what is the specific heat capacity of the metal when the specific heat capacity of water is $4.18 \frac{J}{K\ g}$.

Solution

The formula used to solve this question is

$$m_1 c_1 \Delta T_1 = -m_2 c_2 \Delta T_2$$

Plug in your known values and solve for c_1

$$(34.15\ g)(c_1)(36^\circ C) = -(64\ g)(4.18\ \frac{J}{K\ g})(-14^\circ C)$$

$$c_1 = 3.02\ \frac{J}{K\ g}$$

Q12

A 10.00 g sample of Aluminum at 60.0 °C and a 30.0 g sample of copper at a temperature of -20.0 °C were thrown simultaneously into a 50.0 g of water at a temperature of 25.0 °C. What will be the final temperature of the system consisting of the two metal samples and the water? Assuming that this system is completely isolated from the surroundings. Use the information below for your calculations.

- $c_{s(\text{Al})} = 0.900 J/(K \cdot g)$
- $c_{s(\text{Cu})} = 0.385 J/(K \cdot g)$

- $c_{s(\mathrm{H_2O})} = 4.184 J/(K \cdot g)$

Solution

Since our system is isolated, the thermal energy lost by one component is transferred to the other components.

$$q_1 = -q_2$$

which is equivalent to

$$C_1 \, \Delta T = -C_2 \, \Delta T$$

Noting that

$$C = mC_s$$

To avoid the complexity of handling three components, we can utilize the fact that temperature is a state function; we will simplify our calculations by choosing a different path to arrive to our final state.

We can do this in two steps:

Ignore the Aluminum sample and treat the copper and water as the only components of our system. After finding the equilibrium temperature, we add the Aluminum sample to the water and copper system, thereby reaching the same final state.

Which is the same answer we got before. This should make intuitive sense because regardless of the path we take, we end up with the exact same amount of thermal energy in our system.

Step 1

$$m_{\mathrm{Cu}} \times C_{s(\mathrm{Cu})} \times (T_f - T_{i(\mathrm{Cu})}) = -m_{\mathrm{H_2O}} C_{s(\mathrm{H_2O})} (T_f - T_{i(\mathrm{H_2O})})$$

$$30.0\, g \times 0.385\, J/(^\circ C \cdot g) \times (T_f + 20^\circ C) = -50.0\, g \times 4.184\, J/(^\circ C \cdot g) \times (T_f - 25.0^\circ C)$$

Solving for T_f for the copper and water system gives us

$$T_f = 22.6^\circ C$$

Step 2

$$C_{(\mathrm{Cu+H_2O})} \times (T_f - T_{i(\mathrm{Cu+H_2O})}) = -m_{\mathrm{Al}} \times C_{s(\mathrm{Al})} \times (T_f - T_{i(\mathrm{Al})})$$

Noting that

$$C_{(\mathrm{Cu+H_2O})} = m_{\mathrm{H_2O}} \times C_{s(\mathrm{H_2O})} + m_{\mathrm{Cu}} \times C_{s(Cu)}$$

Combining the two equations and plugging the values gives us

$$[(30.0\, g \times 0.385\, J/(^\circ C \cdot g)) + (50.0\, g \times 4.184\, J/(^\circ C \cdot g))] \times (T_f - 22.6^\circ C) = -10.0\, g \times 0.900\, J/(K \cdot g) \times (T_f - 60^\circ C)$$

Solving for T_f:

$$T_f = 24.1^\circ C$$

Which is the final temperature of the whole system.

Alternative Approach

We can also choose a path where we add the Aluminum first, and then we add the copper. Again, temperature is a state function and choosing a different path will not affect the final answer. We also show the calculation for this path for the sake of completion.

Step 1

$$m_{\mathrm{Cu}} \times C_{s(\mathrm{Al})} \times (T_f - T_{i(Al)}) = -m_{(\mathrm{H_2O})} \times C_{s(\mathrm{H_2O})} \times (T_f - T_{i(\mathrm{H_2O})})$$

$$10.0\, g \times 0.900\, J/(^\circ C \cdot g) \times (T_f + 20^\circ C) = -50.0\, g \times 4.184\, J/(^\circ C \cdot g) \times (T_f - 25.0^\circ C)$$

Solving for T_f for the aluminum and water system gives us

$$T_f = 26.4^\circ C$$

Step 2

$$[(m_{(\mathrm{H_2O})} \times C_{s(\mathrm{H_2O})}) + (m_{\mathrm{Al}} \times C_{s(\mathrm{Al})}))] \times (T_f - T_{i(\mathrm{Al+H_2O})}) = -m_{\mathrm{Al}} \times C_{s(\mathrm{Cu})} \times (T_f - T_{i(\mathrm{Cu})})$$

Plugging the numbers,

$$[(10.0\, g \times 0.900\, J/(^\circ C \cdot g)) + (50.0\, g \times 4.184\, J/(^\circ C \cdot g)] \times (T_f - 26.4^\circ C) = -30.0\, g \times 0.385\, J/(K \cdot g) \times (T_f + 20^\circ C)$$

Solving for T_f

$$T_f = 24.1^{\circ}C$$

Q15A

Calculated the heat required to melt 3.00 g of ice and the heat required to change the temperature of water from 0°C to 100°C. What is the proportionality of the heat necessary to melt ice compared to the heat required to change the temperature of water from 0°C to 100°C? Use values from Table S2 and assume ΔH_f =334 J g^{-1} for calculations? Why is the heat positive instead of negative?

Solution

First lets determine the amount of heat needed to melt ice:

$$q = m\Delta H_f$$

$$q = 1,002 \text{ J}$$

Next lets determine the heat required to raise the temperature of water 100°C:

$$q = mC_s\Delta T$$

$$q = 1,254 \text{ J}$$

So the proportionality was determined to be 4:5

The heat is positive because the heat is required. The heat is needed to make the states go from solid to liquid when melting and then liquid to gas when the temperature is raised from 0 to 100 degrees Celsius.

Q15B

An observation in the 18th century stated that the heat that raised a certain mass of water from its freezing point to boiling point is equal to four-thirds of the heat required to melt the same mass of ice. Using the theory behind the observation, estimate the heat required to melt 10 g of ice, know that the heat capacity of water is 4.18 J/^{o}C.

Solution

Let the heat required to raise the temperature of water from its freezing point to its boiling point is q_1:

$$q = mc\Delta T \tag{12.E.10}$$

$$m = \text{mass} \tag{12.E.11}$$

$$c = 4.18 \frac{J}{g\,^oC} \tag{12.E.12}$$

$$\Delta T = \text{freezing point} - \text{boiling point} = 100 - 0 = 100^oC \tag{12.E.13}$$

$$q_1 = (10g)(4.18 \frac{J}{g\,^oC})(100^oC) \tag{12.E.14}$$

$$q_1 = 4180 \text{ J} = 4.18 \text{ kJ} \tag{12.E.15}$$

Let the heat required to melt 10 g of ice is q_2:

$$q_1 = \frac{4}{3} q_2 \tag{12.E.16}$$

$$q_2 = \frac{3}{4} q_1 \tag{12.E.17}$$

$$q_2 = \frac{3}{4}(4.18 \text{ kJ}) = 3.135 \text{ kJ} \tag{12.E.18}$$

Q17

For his birthday, his John's parents have given him a compressible oven filled with 0.250 mol argon. If he sets this compressible oven at 1.00 atm and 273 K and let it contract from a constant external pressure of 0.100 atm until the gas pressure reaches 10.00 atm and the temperature reaches 400 K, what is the work done on the gas, the internal energy change, and the heat absorbed by the gas?

Solution

Using the ideal gas law $PV = nRT$, we can see that:

$$V_o = \frac{nRT_o}{P_o}$$

$$V_f = \frac{nRT_f}{P_f}$$

n = 0.25 mol, R = 0.082$\frac{atm\ L}{mol\ K}$ Po = 1 atm, Pf = 10 atm To= 273K Tf = 400K

where V_o and V_f represent the initial and final volume of the chamber. Now, the pressure clearly changes inside the chamber, but outside the chamber, the pressure is held constant, so from the perspective of the surroundings:

$$W = -P(V_f - V_o)$$

where P represents the constant external pressure. Now substituting in V_f and V_o we can see that we've solved for work. Now, for any thermodynamic process:

$$\Delta U = \frac{3}{2}nR(T_f - T_o)$$

So plugging in those values allows us to solve for ΔU. Now, for heat, we simply subtract W from ΔU, by the first law of thermodynamics.

First law of thermodynamics: the total energy of an isolated system is a constant, energy can be transformed from one form to another, but it can not be created or destroyed.

The solution is incomplete.

Q19

Take 4 moles of ideal, monatomic gas going through expansion processes. The gas was initially put at a pressure of 5.00 atm and a temperature of 30°C. The gas first goes through isothermal expansion until the volume doubled. An isochoric process follows as the pressure is halved. $C_v = \frac{3}{2}R$

a. Build ΔU, W, and Q table for each process.
b. Find the final temperature.

Solution

Isothermal Process:

$$\Delta U = 0 \tag{12.E.19}$$

$$W = Q \tag{12.E.20}$$

$$W = nRT\ln\left(\frac{V_f}{V_i}\right) = (4\,\text{mol})(8.314\,\text{J}\cdot\text{K}^{-1}\text{mol}^{-1})(303.15\,\text{K})\ln(2) = 6988\,\text{J} = Q \tag{12.E.21}$$

Isochoric Process

$$W = 0 \tag{12.E.22}$$

$$\Delta U = Q \tag{12.E.23}$$

First find the initial pressure of this process.

Use ideal law to relate pressure to volume. $PV = nRT$, in which P is inversely proportional to V.

Thus, when volume is doubled, pressure is halved so $P_f = 2.50\,\text{atm}$. Now, find the final temperature of this process.

Once again, relate P to T using ideal gas law. T is found to be directly proportional to P. Thus, if the pressure is halved from 2.50 atm, the temperature must also be halved from 303.15K.

$\frac{1}{2}(303.15\,\text{K}) = 151.58\,\text{K}$

$$Q = nC_v\Delta T = (4.00\,\text{mol})(\frac{3}{2})(8.314\frac{\text{J}}{\text{K mol}})(-151.58K) = -7561\,\text{J} = \Delta U \tag{12.E.24}$$

Processes	ΔU	Q	W
Isothermal	0	6988J	6988J
Isochoric	-7561J	-7561J	0

Q20

An apparatus is set up such that an ideal gas is released into vacuum by opening a stopcock, hence allowing it to freely expand (i.e., no external force is applied). Calculate ΔU of the system, and prove that the free expansion process is adiabatic i.e no heat transfer.

Solution

$$\Delta U = \frac{3}{2}nR\Delta T \tag{12.E.25}$$

As the expansion is isothermal, i.e. it occurs without a change in temperature:

$$\Delta T = 0 \tag{12.E.26}$$

Hence,

$$\Delta U = 0 \tag{12.E.27}$$

and

$$\Delta U = q_p + w \tag{12.E.28}$$

As the external force applied on the gas is zero, the work done by the gas is zero.

Hence,

$$0 = q_p + 0 \tag{12.E.29}$$

$$q_p = 0 \tag{12.E.30}$$

This proves that the process is adiabatic.

Q21

A 150 L vessel contains 8.00 moles of neon at 270 K is compressed adiabatically, so that there is no gain nor loss of any heat, and irreversibly until the final temperature is 470 K. Calculate the change in internal energy, the heat added to the gas, and the work done on the gas.

Solution

Since Ne is a monatomic ideal gas and the volume of the vessel remains constant, the heat capacity of Ne can be expressed as:

$$C_p = \frac{3}{2} \times R = \frac{3}{2} \times 8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}} = 12.47 \frac{\text{J}}{\text{K} \cdot \text{mol}} \tag{12.E.31}$$

$$\Delta U = nC_p \Delta T \tag{12.E.32}$$

$$\Delta U = 8.00 \times 12.47 \frac{\text{J}}{\text{K} \cdot \text{mol}} \times (470 - 2700)\ \text{K} = 19952\ \text{J} = 20.0\ \text{kJ} \tag{12.E.33}$$

Since the vessel is adiabatically compressed, no heat is added, therefore $q = 0$

$$\Delta U = q + w \tag{12.E.34}$$

$$20.0\ \text{kJ} = 0 + w \tag{12.E.35}$$

$$w = 20.0\ \text{kJ} \tag{12.E.36}$$

Q22

A gas expands at constant external pressure of 3.00 atm until its volume has increased by 9.00 to 15.00 L. During this process, it absorbs 800J of heat from the surroundings.

a. Calculate the energy change of the gas, ΔU
b. Calculate the work, *w*, done on the gas in an irreversible adiabatic (*q* = 0) process connecting the same initial and final state.

Solution

a)

$$\Delta U = q + w \tag{12.E.37}$$

$$\Delta U = 800J + -((3.00\,\text{atm})(15.00\text{L} - 9.00\text{L})(101.3 \frac{\text{J}}{\text{L atm}})) = -1023.4\text{J} \tag{12.E.38}$$

b)

$$q = 0 \tag{12.E.39}$$

$$\Delta U = w \tag{12.E.40}$$

$$\Delta U = -((3.00\text{atm})(15.00\text{L} - 9.00\text{L})(101.3 \frac{\text{J}}{\text{L atm}})) = -1823.4\text{J} \tag{12.E.41}$$

Q23

Using the theorem of equipartition of energy, calculate the specific heat capacity at constant pressure C_p at 25ºC and 1 atm for O_2 and CO. Compare the calculated values to the experimental data $(\text{O}_2 = 29.36, \text{CO} = 29.1)$ and thus calculate the percent of the experimental value that results from vibrational motions. Answer: The percent of C_p due to vibrational motions is 0.897% for O_2 and 0.141% for CO.

Solution

The equipartition theorem states that each degree of freedom in a molecule contributes to ½ RT to the molar internal energy of a gas. To solve this problem, the number of degrees of freedom DOF in each molecule must be identifies.

O_2 is a linear diatomic particle, thus it has 3 translational degrees of freedom and 2 rotational degrees of freedom. Since CO is a linear molecule it also has 3 translational and 2 rotational degrees of freedom. The molecules are at room temperature. Thus, it is assumed that there is no vibration in the bond (other than the zero point energy).

The low percentage of C_p due to vibrational modes in both molecules indicates that the vibrational motion is extremely small and can be neglected.

$$DOF(\mathrm{O_2}) = f_t + f_r = 3 + 2 = 5$$

$$DOF(\mathrm{CO}) = f_t + f_r = 3 + 2 = 5$$

Using the equation

$$U = (DOF) \cdot \left(\frac{1}{2}RT\right)$$

find the internal energy of each gaseous molecule.

$$U\left(\mathrm{O_2}\right) = (5) \cdot \left(\frac{1}{2}RT\right)$$

Since O_2 and CO have the same degrees of freedom,

\[U\left(\ce{O_2} \right) = U\left(\ce{CO} \right) = \dfrac{5}{2}RT\nonumber \]

The internal energy is related to C_v by

$$C_v = \left(\frac{\partial U}{\partial T}\right) = \left(\frac{\partial \frac{5}{2}RT}{\partial T}\right) = \frac{5}{2}R$$

C_v is related to C_p by

$$C_p = C_v + R = \frac{5}{2}R + R = \frac{7}{2}R = \frac{7}{2} \times 8.314 \frac{J}{mol\ K} = 29.099 \frac{J}{mol\ K}$$

The percent of the experimental value that results from vibration motion is the difference between calculated and experimental value as a percentage of the experimental value.

$$\%\text{vibrational motion}(\mathrm{O_2}) = \frac{\text{experimental value} - \text{calculated value}}{\text{experimental value}} \times 100\% = \frac{29.36 - 29.099}{29.099} \times 100\% = 0.897\%$$

$$\%\text{vibrational motion}(\mathrm{CO}) = \frac{\text{experimental value} - \text{calculated value}}{\text{experimental value}} \times 100\% = \frac{29.14 - 29.099}{29.099} \times 100\% = 0.141\%$$

Q23B

Using the classical equipartition theorem, calculate the value of C_p at 298 K and 1 atm for $\mathrm{HF}(g)$ and $\mathrm{F_2}(g)$, assuming that their pressure is constant. Then compare your calculation with the experiment values of $29.13 \frac{\mathrm{J}}{\mathrm{K\ mol}}$ and $31.30 \frac{\mathrm{J}}{\mathrm{K\ mol}}$respectively. What is the per cent of the measured value that arises from vibrational motions?

Solution

Diatomic molecules possess a total of 6 degrees of freedom:

- 3 degrees in **translational** motion
- 2 degrees in **rotational** motion
- 1 degree in their **vibrational** motions

$$6.11 \text{ for } \mathrm{F_2}(g) = 0.735R \tag{12.E.42}$$

The differences are due to the fact that some quantized energy levels are not available at certain temperatures, in this case room temperature. This means that $\mathrm{HF}_{(g)}$ contributed only 0.004R of its experimental value of $29.13 \frac{\mathrm{J}}{\mathrm{K\ mol}}$to the vibrational degree of freedom, which is 0.014%. F2 (g) contributed 0.265R of its experimental value $31.30 \frac{\mathrm{J}}{\mathrm{K\ mol}}$, which is 0.847%.

Each translational and rotational degree of freedom contributes $\frac{R}{2}$ to the heat capacity of a gas, while each vibrational degree of freedom contributes $\frac{2R}{2}$ (=R). Therefore the predicted heat capacity (C_v) at a constant volume is:

$$C_v = 3 \times (\frac{R}{2}) + 2 \times (\frac{R}{2}) + 1 \times (\frac{2R}{2}) = 7(\frac{R}{2}) \tag{12.E.43}$$

Since the question is asking for the heat capacity of these gases that are under a constant pressure, the result is multiplied by an additional $\frac{2R}{2}$ because the volume can change in order to keep the pressure constant. Therefore:

$$C_v = (\frac{2R}{2}) + (\frac{7R}{2}) = \frac{9R}{2} \tag{12.E.44}$$

$$R = 8.3145 \frac{\text{J}}{\text{K mol}} \tag{12.E.45}$$

$$C_p = \frac{9(8.3145 \frac{\text{J}}{\text{K mol}})}{2} = 37.41 \frac{\text{J}}{\text{K mol}} \tag{12.E.46}$$

This is the calculated value for both of the two gases. Since the experiment values were $29.13 \frac{\text{J}}{\text{K mol}}$ for $\text{HF}(\text{g})$ and $31.30 \frac{\text{J}}{\text{K mol}}$ for $\text{F}_2(\text{g})$, the differences between the calculations were:

$$8.28 \text{ for HF}(\text{g}) = 0.996R \tag{12.E.47}$$

Q25

a. Calculate the change of enthalpy when a 69-grams sample of zinc is heated from 753 K to 927 K at a constant pressure of 1 atm.
b. Calculate the change of enthalpy when 3 moles of butane are heated from 204 K to 258 K at a constant pressure of 1 atm.

Solution

a)

$q = mC_s \Delta T$

$m = 69 \text{ g}$

$\Delta T = 927 - 753 = 174 \text{ K}$

$C_{\text{s(zinc)}} = 0.39 \frac{\text{J}}{\text{g }^{\circ}\text{C}}$

$q = 69 \times 0.39 \times 174 = 4682.34 \text{ J} = 4.56 \text{ kJ}$

b)

$q = nC_p \Delta T$

$n = 3$

$\Delta T = 258 - 204 = 54 \text{ K}$

$C_p = 132.42$

$q = 3 \times 132.42 \times 54 = 21452.04 \text{ J} = 21.4504 \text{ kJ}$

Q31

What is the change in enthalpy when 8.19 grams of ethane (C_2H_6) vaporizes, assuming a normal boiling point and $\Delta H_{\text{vap}} = 14.72 \frac{\text{kJ}}{\text{mol}}$.

Solution

First, convert grams of ethane to moles:

$$(8.19 \ \cancel{g\ \text{C}_2\text{H}_6}) \left(\frac{1\ mol}{30.07 \ \cancel{g\ \text{C}_2\text{H}_6}} \right) = 0.272\ mol$$

This step is to match quantity units of ethane to those in the given value of $\Delta\text{H}_{\text{vap}}$.

Then, given the ΔH_{vap},

$$(0.272 \ \cancel{mol\ \text{C}_2\text{H}_6}) \left(\frac{14.72\ kJ}{1 \ \cancel{mol\ \text{C}_3\text{H}_8}} \right) = 4.004\ kJ$$

$\Delta\text{H} = 4.004\ kJ$

This value is the change in enthalpy, or thermodynamic energy, when the specified amount of ethane undergoes the above reaction.

Q33

The heat capacity C_p of ice is $38\dfrac{\text{J}}{\text{K mol}}$ and C_p of water is $75\dfrac{\text{J}}{\text{K mol}}$. A 24.0 g ice cube at -15 ^{o}C is placed into 120 g of water at room temperature (25^{o}C). What is the temperature of the water when it reaches equilibrium?

Solution

$$q_{\text{ice}} = -q_{\text{water}} \tag{12.E.48}$$

$$m_{\text{ice}}C_{\text{ice}}(T_f - T_{\text{ice}}) = -m_{\text{water}}C_{\text{water}}(T_f - T_{\text{water}}) \tag{12.E.49}$$

$$\left(\frac{24g\,\text{ice}}{18.02\dfrac{g}{mol}}\right) \times (38\frac{J}{K\ mol}) \times (T_f - (-15^oC)) = -\left(\frac{120g\,\text{water}}{18.02\dfrac{g}{mol}}\right) \times (75\frac{J}{K\ mol}) \times (T_f - 25^oC) \tag{12.E.50}$$

$$T_f = 21.316^oC \tag{12.E.51}$$

Q35

Determine the change in enthalpy (ΔH) for the following chemical reaction

$4\,NH_{3\,(g)} + 5\,O_{2\,(g)} \longrightarrow 4\,NO_{(g)} + 6\,H_2O_{(g)}$

given that:

$O_{2\,(g)} + N_{2\,(g)} \longrightarrow 2\,NO_{(g)} \quad \Delta H = +180.5\ \dfrac{\text{kJ}}{\text{mol}}$

$2\,H_2O_{(g)} \longrightarrow 2\,H_{2\ (g)} + O_{2\ (g)} \quad \Delta H = +483.64\ \dfrac{\text{kJ}}{\text{mol}}$

$3\,H_{2\,(g)} + N_{2\,(g)} \longrightarrow 2\,NH_{3\,(g)} \quad \Delta H = -92.22\ \dfrac{\text{kJ}}{\text{mol}}.$

Solution

Using Hess's Law, we can obtain the ΔH for

$$4\,NH_{3\,(g)} + 5\,O_{2\,(g)} \rightleftharpoons 4\,NO_{(g)} + 6\,H_2O_{(g)}$$

by adding and modifying the other equations provided until they resemble the equation above.

$(O_{2(g)} + N_{2(g)} \rightleftharpoons 2NO_{(g)}) \times (2) \quad \Delta H = +180.5\ \dfrac{kJ}{mol} \times (2)$

$(2H_2O_{(g)} \rightleftharpoons 2H_{2\,(g)} + O_{2\,(g)}) \times (-3) \quad \Delta H = +483.64\ \dfrac{kJ}{mol}(-3)$

$(3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}) \times (-2) \quad \Delta H = -92.22\ \dfrac{kJ}{mol} \times (-2)$

The above modifications simplify out to

$2\,O_{2\,(g)} + 2\,N_{2\,(g)} \rightleftharpoons 4\,NO_{(g)} \quad \Delta H = +361.0\ \dfrac{kJ}{mol}$

$6\,H_{2\ (g)} + 3\,O_{2\ (g)} \rightleftharpoons 6\,H_2O_{(g)} \quad \Delta H = -1450.92\ \dfrac{kJ}{mol}$

$4\,NH_{3\ (g)} \rightleftharpoons 6\,H_{2\ (g)} + 2\,N_{2\ (g)} \quad \Delta H = 184.4\ \dfrac{kJ}{mol}$

Species that are common to both sides can be cancelled out.

$2\,O_{2\,(g)} + \cancel{2\,N_{2\,(g)}} \rightleftharpoons 4\,NO_{(g)} \quad \Delta H = +361.0\ \dfrac{kJ}{mol}$

$\cancel{6\,H_{2\ (g)}} + 3\,O_{2\ (g)} \rightleftharpoons 6\,H_2O_{(g)} \quad \Delta H = -1450.92\ \dfrac{kJ}{mol}$

$4\,NH_{3\ (g)} \rightleftharpoons \cancel{6\,H_{2\ (g)}} + \cancel{2\,N_{2\ (g)}} \quad \Delta H = 184.4\ \dfrac{kJ}{mol}$

Finally, after adding the remaining specimens and the enthalpy change that occurs with them we have:

$4\,NH_{3\,(g)} + 5\,O_{2\,(g)} \rightleftharpoons 4\,NO_{(g)} + 6\,H_2O_{(g)}$ with $\Delta H = -905.5\ \dfrac{kJ}{mol}$

Q37

ΔH of $C_6H_6(g)$ from $C_6H_6(l)$ to its gaseous form is +33.9 kJ/mol. Which of these two substances absorbs off more heat when 10 lbs of the substance is burned? Which of these two substances require less energy when condensed to solid form?

Solution

An alternative way to view this is to inspect the reactions under comparison

$$2\,C_6H_6(g) + 15\,O_2(g) \longrightarrow 12\,CO_2(g) + 6\,H_2O(g)$$

vs.

$$2\,C_6H_6(l) + 15\,O_2(g) \longrightarrow 12\,CO_2(g) + 6\,H_2O(g)$$

Recognizing that the difference between these equations is

$$2\,C_6H_6(l) \longrightarrow 2\,C_6H_6(g)$$

The problem states that the ΔH of the conversion of $C_6H_6(g)$ to $C_6H_6(l)$ is positive, and therefore, is an endothermic process. Consequently, ten pounds of $C_6H_6(g)$ contains more enthalpy than 10 pounds of $C_6H_6(l)$. Since these will both produce carbon dioxide and water when burned, their products are of the same final energy level. As a result, $C_6H_6(g)$ will give off more energy than $C_6H_6(l)$ when burned and $C_6H_6(l)$ will require less energy to form a solid.

Q39

Calculate the enthalpy change under standard conditions for the reaction:

$$C_3H_6O(l) + 4\,O_2(g) \rightarrow 3\,CO_2(g) + 3\,H_2O(l)$$

given information below:

- $\Delta H°_{f,\ O_2(g)}$: 0 kJ/mol
- $\Delta H°_{f,\ CO_2\,(g)}$: -393.5 kJ/mol
- $\Delta H°_{f,\ H_2O(l)}$: -285.83 kJ/mol
- $\Delta H°_{f,\ C_3H_6O(l)}$: -248 kJ/mol

Solution

Hess' Law:

$$\Delta H^o_{rxn} = \sum \Delta H^o_{f,\,products} - \sum \Delta H^o_{f,\,reactants}$$

$\Delta H°_{rxn}$ = [**3** (-393.5 kJ/mol) + **3** (-285.83 kJ/mol)] - [(-248 kJ/mol) + **4** (0 kJ/mol)] = -1790 kJ/mol

Q47

A 10 gram sample of pure hydrogen is burned completely with excess oxygen to generate liquid water in a constant volume calorimeter at 25 °C. The amount of heat evolved is 1,420 kJ.

a. Write and balance the chemical equation for the combustion reaction.
b. Calculate the standard change in internal energy for the combustion of 1.00 mole hydrogen to liquid water.
c. Calculate the standard enthalpy change per mole of hydrogen for the same reaction as in part (a).
d. Calculate the standard enthalpy of formation per mole of hydrogen, using data for the standard enthalpies of formation of liquid water (Table T1).

Solution

a. $2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$
b. $\Delta U^o = q_v = \dfrac{-1420\,kJ}{10/(1.008 \times 2)g/mol} = -286.3\,kJ/(mol\,of\,H_2)$
c. $\Delta H^o_{rxn} = \Delta U^o + \Delta n_{gas}RT = -286.3\,kJ/(mol\,of\,H_2) + (2mol.\ of\ H_2)(-3)(8.314J/K/mol)(298\,K) = -580\,kJ/mol$
d. $\Delta H^o_r xn = 2\Delta H^o_f\{H_2\}$ so $\Delta H^o_f/2$.

A consequence of the constant-volume condition is that the heat released corresponds to q_v and thus to the internal energy change ΔU_{sys} rather than to ΔH_{sys} under constant pressure conditions.

$$\Delta U_{sys} = q_v$$

This comes from the definition of enthalpy

$$H_{sys} = U_{sys} + PV$$

and associated change

$$\Delta H_{sys} = \Delta U_{sys} + \Delta(PV)$$

or using the chain rule

$$\Delta H_{sys} = \Delta U_{sys} + P\cancel{\Delta V}^{0} + V\Delta P$$

which simplifies to

$$\Delta H_{sys} = \Delta U_{sys} + V\Delta P$$

If we assuming ideal gas law for the gases

$$PV = nRT$$

or

$$\Delta P = \frac{\Delta nRT}{V}$$

substituting this into the equation for enthalpy change gives the enthalpy change under *constant volume* conditions in terms of changing number of moles

$$\Delta H_{sys} = \Delta U_{sys} + \Delta n_g RT$$

or

$$\Delta H_{sys} = q_v + \Delta n_g RT$$

where Δn_g is the change in the number of moles of gases in the reaction.

Q49

Carbon dioxide (CO_2) is a common byproduct of the combustion of fossil fuels. Estimate the standard enthalpy of formation (ΔH_f) of carbon dioxide at 25°C, use Table T1.

Solution

First write the equation:

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

The bond enthalpies in Table T3 allows us to calculate ΔH° because 2 C=O and 2 C-O bonds are formed:

$$\Delta H^\circ \approx 2 \text{ mol } (-192.0 \text{ kJ mol}^{-1}) + 2 \text{ mol } (-85.5) = -555 \text{ kJ}$$

Next we need to write the equations for "striping" the atoms from there standard state to single atoms. Each of the atomization has an enthalpy that was found in Table T1:

$$C(s) \longrightarrow C(g)$$

$$\Delta H^\circ = 1 \text{ mol } (716.7 \text{ kJ mol}^{-1}) = 716.7 \text{ kJ}$$

$$O_2(g) \longrightarrow 2\,O(g)$$

$$\Delta H^\circ = 2 \text{ mol } (249.2 \text{ kJ mol}^{-1}) = 498.4 \text{ kJ}$$

Combine the results of all three equations to calculate ΔH_f of 1 mol of CO_2:

$$-555 \text{ kJ} + 716.7 \text{ kJ} + 498.4 \text{ kJ} = 660.1 \text{ kJ}$$

This solution should be the same if finding the standard enthalpy of formation by using Table T1 which would be -393.5 kJ for one mole of CO_2. Since this question is not clear, it is better if the students answering this question to just use Table T1 which will just use the standard heat of formation for and then have the sum of products minus the sum of reactants = the answer. So the answer would be -393.5 kJ.

Q51

Given the table of average bond enthalpies shown below, estimate the enthalpy change ΔH° for the following reaction:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$$

Bond	Bond Enthalpy (kJ/mol)
H−H	436
H−O	463
O=O	498

Solution

To calculate the total enthalpy change of the reaction, we use Hess's Law. Thus, the total enthalpy of formation is equal to the sum of the enthalpy of formation of the reactants and the enthalpy of formation for the products.

Step 1. ΔH_1 = the bond enthalpies of $2\,\mathrm{H_2(g)} + \mathrm{O_2(g)}$

$$\begin{aligned} &= 2(\mathrm{H{-}H}) + (\mathrm{O{=}O}) \\ &= 2(436)\ \mathrm{kJ/mol} + 498\ \mathrm{kJ/mol} \\ &= +1370\ \mathrm{kJ/mol} \end{aligned}$$

Step 2. ΔH_2 = the bond enthalpies of $2\mathrm{H_2O}(l)$

$$\begin{aligned} &= 2 \times 2(\mathrm{H{-}O}) \\ &= 4(463)\ \mathrm{kJ/mol} \\ &= -1852\ \mathrm{kJ/mol} \end{aligned}$$

Step 3. $\Delta H^\circ = \Delta H_1 + \Delta H_2$

$$\begin{aligned} &= 1370\ \mathrm{kJ/mol} - 1852\ \mathrm{kJ/mol} \\ &= -482\ \mathrm{kJ/mol} \end{aligned}$$

Note in Step 1, ΔH_1 is positive because the process of breaking the bonds into individual atoms is ***always*** *an endothermic process while in Step 2, ΔH_2 is negative because the process of creating bonds out of the individual atoms is* ***always*** *an exothermic process.*

Q59

Two quantum states are separated by an energy of 0.6 × 10^{-21}J. Calculate the relative populations of the two quantum states at a temperature of 33°C.

Solution

The equation for the relative populations of two quantum states, P_2/P_1 is given by the equation

$$\frac{P_2}{P_1} = e^{-(E_2-E_1)/k_BT}$$

Where E_2-E_1 is the energy difference between the two states, k_B is the Boltzmann constant, and T is the temperature.

Plug in the given values into the equation to reach the final answer.

$$\frac{P_2}{P_1} = e^{-(0.6\cdot 10^{-21}\,\mathrm{J})/1.38\cdot 10^{-23}\mathrm{K}^{-1}(298\,\mathrm{K}))}$$

$$\frac{P_2}{P_1} = 0.86$$

Q63

By utilizing the Harmonic Oscillator Model, calculate the relative population of the first energy state and the ground state, both at $278.15\ \mathrm{K}$, for $\mathrm{H_2}$. The force constant for $\mathrm{H_2}$ is $510\frac{\mathrm{N}}{\mathrm{m}}$

Solution

A few pieces of information need to be understood before going about solving this equation. First, the question asks for the “relative population” of the first energy state at a given temperature ($278.15\ \mathrm{K}$) to the energy state at $0\ \mathrm{K}$. Recall that energy states are basically a way of saying that every chemical species (molecule, atom, etc.) can “have” a specific (discreet) amount of energy. Each of these values are a “state”, and the lowest- value state can be considered the “ground state”, and all states above are “excited states”. Also recall that the states can be named by quantum number; i.e if n were the quantum number, than the ground state would be $n = 0$ and the first state after that, an excited state, has a quantum number $n = 1$. The next step is to understand what “relative population is”. Basically, this refers to the probability that the species, in this case $\mathrm{H_2}$, will be found in one energy state versus another. The equation that describes the probability of a species being in energy level n is as follows:

$P(n) = Ce^{-\varepsilon_n/k_bT}$

Where C is a constant, n is quantum number (energy level), k_b is Boltzmann’s constant, T is temperature, and ε is the energy of the molecule, which can be determined as such:

$$\varepsilon_n = \left(n + \frac{1}{2}\right) hv$$

$$hv = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

n, as already seen, is the quantum number. hv in the equation for ε is defined as the product of planck's constant (h) divided by 2π and the $\sqrt{\frac{k}{\mu}}$, where k is the force constant, which is given in the problem, and the μ is the *reduced mass*, which can be calculated as follows:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Where m is just the mass of each of the atoms. Since the mass of both hydrogens are 1 amu (u),

$$\mu = \frac{1 \times 1}{1+1} = \frac{1}{2}u$$

$$\frac{1}{2}u = 8.3027 \times 10^{-28} kg$$

Because the question is only interested in *relative* population, the actual number of molecules there are doesn't really matter, since *relative* means to take the ratio between the probability of one energy state to another. Since the two energy states in comparison for this problem is $n=1, n=0$, (remember ground state is $n=0$), the equation is as follows.

$$\frac{P(1) = Ce^{-\varepsilon_1/k_b 278.15\text{ K}}}{P(0) = Ce^{-\varepsilon_0/k_b 278.15\text{ K}}}$$

By simplification,

$$= e^{\frac{\varepsilon_1 - \varepsilon_0}{K_b T}}$$

And, substituting in the formula for energy(ε),

$$= e^{\frac{\left[\left(n+\frac{1}{2}\right) hv - \frac{1}{2}hv\right]}{K_b T}}$$

$$= e^{nhv/K_b T}$$

Here, $n=1$ (because the 0 has already been taken into consideration) and hv is as follows:

$$hv = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$hv = \frac{6.62607 \times 10^{-34} \frac{kgm^2}{s^2}}{2\pi}\sqrt{\frac{510\frac{N}{m}}{8.3027 \times 10^{-28} kg}}$$

$$hv = \frac{6.62607 \times 10^{-34} Js^{-1}}{2\pi}\sqrt{\frac{510\frac{N}{m}}{8.3027 \times 10^{-28} kg}}$$

$$hv = 8.2650 \times 10^{-20} J$$

All the variables have been found, so all there is left is to substitute and solve.

$$= e^{\frac{-(1)\left(8.2650 \times 10^{-20} J\right)}{1.3806 \times 10^{-23} \frac{m^2 kg}{s^2 K}(278.15K)}}$$

$$= e^{\frac{-(1)\left(8.2650 \times 10^{-20} J\right)}{1.3806 \times 10^{-23} \frac{J}{K}(278.15K)}}$$

$$\approx e^{-21.5229}$$

$$\approx 4.495 \times 10^{-10}$$

Thus, the probability of the H_2 molecules being in the 1st energy state when compared to the vibrational state of the lowest energy is $\approx 4.495 \times 10^{-10}$. This extremely low probability makes sense, because intuition says that the compound will most likely be found at its lowest energy.

Abstract: Find difference in energy, ε, divide by Boltzmann's constant (K_b) and Temperature. Plug as e^x and solve.

Q69

A container holds 2 L of gas under 5.00 atm and a ball floating in 10 L of NaOH. As the volume of the gas expands to 20 L, the ball is turned upside down. This turn is caused by the temperature increase of the NaOH after the gas expands. Assuming that no heat is lost, the density of NaOH is 2.13

g/cm^3 and the specific heat is 4.184 J/g K, calculate the increase in temperature of the NaOH.

Solution

The "work" completed by the ball to turn equals the negative value of the work the gas absorbs.

w = -(-P (V$_2$-V$_1$))

w = -(-5 atm) (20-2) L

w = 90 atm L (101.325 J/ 1 atm L)

w = 9119.25 J

The work carried out by the ball by the NaOH (in order to turn the ball) correlates to the increase in 10 L of NaOH temperature .

10 L of NaOH (1000 mL/1 L) = 10000 mL = 10000 cm^3 (2.13 g/cm^3) = 21300 g of NaOH

q = mC$_p$ΔT

ΔT = (q NaOH) / (Specific Heat NaOH * g NaOH)

ΔT = (9119.25 J) / (4.184 J/K g)(21300 g)

ΔT = 0.102 K gained by the NaOH to turn the ball

Q69

Some gas in a piston expands against a constant pressure of 1.2 atm from a volume of 3 L to 18 L. The piston turns an egg beater submerged in 150 g of water. If the water was originally at 25°C, what is its temperature once the gas stops expanding? Assume that all of heat goes into the water and the specific heat capacity of water is 4.184 J K^{-1} g^{-1}.

Solution

From the first law of thermodynamics

$$\Delta U = q + w$$

In this case, $\Delta U = 0$, so

$$q = w = P_{ext}\Delta V = P_{ext}(V_f - V_i)$$

$$q = (1.2 \text{ atm})(18 \text{ L} - 3 \text{ L}) = 14.4 \text{ L atm}$$

Convert From L atm to joules using the conversion factor

$$14.4 \text{ L atm} \times 101.325 \text{ J L}^{-1}\text{atm}^{-1} = 1459 \text{ J}$$

Now connect the heat transferred to the temperature increased via the specific heat c_{sp} via

$$q = mc_{sp}\Delta T$$

$$\Delta T = \frac{q}{mc_{sp}}$$

$$\Delta T = \frac{1459 \text{ J}}{(150 \text{ g})(4.184 \text{ J K}^{-1}\text{g}^{-1})} = 2.325 \text{ K}$$

Since initial temperatures is 25° = 298 K so

$$T_f = 298\ K + 2.325 \text{ K}$$

$$T_f = 300.325\ K = 27.325^\circ\text{C}$$

CHAPTER OVERVIEW

13: Spontaneous Processes and Thermodynamic Equilibrium

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

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A spontaneous process is the time-evolution of a system in which it releases free energy and moves to a lower, more thermodynamically stable energy state.

13.1: The Nature of Spontaneous Processes

Learning Objectives

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

In this section, consider the differences between two types of changes in a system: Those that occur spontaneously and those that occur only with the continuous input of energy. In doing so, we'll gain an understanding as to why some systems are naturally inclined to change in one direction under certain conditions. We'll also gain insight into how the spontaneity of a process affects the distribution of energy and matter within the system.

Spontaneous and Nonspontaneous Processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. A spontaneous process is one that occurs naturally under certain conditions. A nonspontaneous process, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure $13.1.1$).

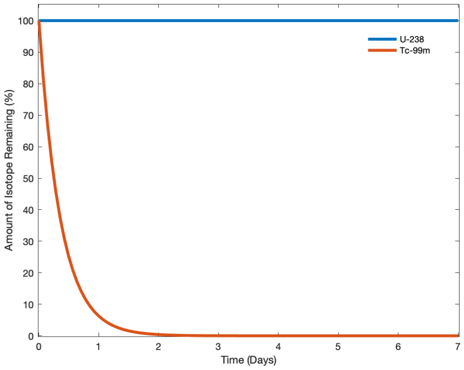

Figure 13.1.1: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts)

Two curves are shown to represent U-238 and Tc-99m respectively. The vertical axes represents the percentage of isotope remaining and the horizontal axes is the time that has elapsed in days.

As another example, consider the conversion of diamond into graphite (Figure $13.1.2$).

$$\mathrm{C(s, diamond)} \longrightarrow \mathrm{C(s, graphite)} \tag{13.1.1}$$

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow, and so for all practical purposes diamonds are indeed "forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

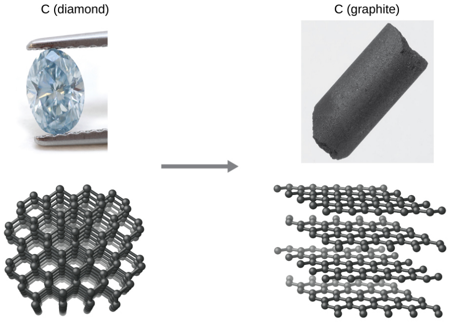

Figure 13.1.2: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

Comparison of diamond and graphite shown in its physical form as well as its molecular arrangement respectively.

Dispersal of Matter and Energy

As we extend our discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas on the left and a vacuum on the right (Figure $13.1.3$). When the valve is opened, the gas spontaneously expands to fill both flasks. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

$$w = -P\Delta V \tag{13.1.2}$$

$$= 0 \quad (\mathrm{P = 0 \; in \, a \; vaccum}) \tag{13.1.3}$$

Note as well that since the system is isolated, no heat has been exchanged with the surroundings (q = 0). The first law of thermodynamics confirms that there has been no change in the system's internal energy as a result of this process.

$$\begin{aligned} \Delta U &= q + w \qquad \text{(First Law of Thermodynamics)} \\ &= 0 + 0 = 0 \end{aligned} \tag{13.1.4}$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the movement of the gas appears to be related to the greater, more *uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous process took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

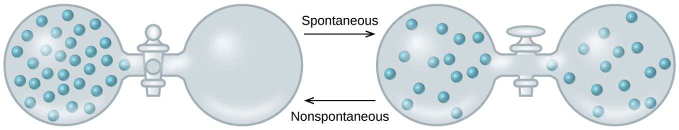

Figure 13.1.3: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

When the valve is closed, all of the gas molecules accumlating only in one side of the flask. The diagram with the open valve shows gas being equally distributed among the two flasks. The dispersion of the gas is labeled as spontaneous while the reverse is labeled as non spontaneous.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure 13.1.4). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0 \tag{13.1.5}$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.

Figure 13.1.4:When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

Two separated blocks. One is labeled X and the other labeled Y. The diagram next to it shows the two blocks in contact with one another.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

✓ Example 13.1.1: Redistribution of Matter during a Spontaneous Process

Describe how matter and energy are redistributed when the following spontaneous processes take place:

a. A solid sublimes.
b. A gas condenses.
c. A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution


(a) (b) (c)

Figure 13.1.5:(credit a: modification of work by Jenny Downing; credit b: modification of work by "Fuzzy Gerdes"/Flickr; credit c: modification of work by Sahar Atwa)

This figure has three photos labeled, "a," "b," and "c." Photo a shows a glass with dry ice in water. There is a thick vapor coming from the top of the glass. Photo b shows water forming outside of a glass containing cold beverage. Photo c shows a sealed container that holds a red liquid.

a. *Sublimation* is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition. However, an input of energy from the surroundings ss required for the molecules to leave the solid phase and enter the gas phase.
b. *Condensation* is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition. As the gas molecules move together to form the droplets of liquid, they form intermolecular forces and thus release energy to the surroundings.
c. The process in question is *dilution*. The food dye molecules initially occupy a much smaller volume (the drop of dye solution) than they occupy once the process is complete (in the full glass of water). The process therefore entails a greater dispersal of matter. The process may also yield a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop, zero in the water), and the final state of the system contains a single dye concentration throughout. This process can occur with out a change in energy because the molecules have kinetic energy relative to the temperature of the water, and so will be constantly in motion.

? Exercise 13.1.1

Describe how matter and energy are redistributed when you empty a canister of compressed air into a room.

Answer

This process entails both a greater and more uniform dispersal of matter as the compressed air in the canister is permitted to expand into the lower-pressure air of the room. The process also requires an input of energy to disrupt the intermolecular forces between the closely-spaced gas molecules that are originally compressed into the container. If you were to touch the nozzle of the canister, you would notice that it is cold because the exiting molecules are taking energy away from their surroundings, and the canister is part of the surroundings.

Summary

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will experience a change in the way matter and/or energy is distributed within the system. In this section we have only discussed nuclear decay, physical changes of pure substances, and macroscopic events such as water flowing downhill. In the following sections we will discuss mixtures and chemical reactions, situations in which the description of sponteneity becomes more challenging.

Glossary

nonspontaneous process
process that requires continual input of energy from an external source

spontaneous change
process that takes place without a continuous input of energy from an external source

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13.2: Entropy and Spontaneity - A Molecular Statistical Interpretation

Learning Objectives

- The Learning Objective of this Module is to understand the relationship between internal energy and entropy.

We know that the first law of thermodynamics governs changes in the state function we called internal energy (U) and that changes in the internal energy (ΔU) are closely related to changes in the enthalpy (ΔH), which is a measure of the heat flow between a system and its surroundings at constant pressure. You also learned previously that the enthalpy change for a chemical reaction can be calculated using tabulated values of enthalpies of formation. This information, however, does not tell us whether a particular process or reaction will occur spontaneously.

Spontaneous Reactions

Let's consider a familiar example of spontaneous change. If a hot frying pan that has just been removed from the stove is allowed to come into contact with a cooler object, such as cold water in a sink, heat will flow from the hotter object to the cooler one, in this case usually releasing steam. Eventually both objects will reach the same temperature, at a value between the initial temperatures of the two objects. This transfer of heat from a hot object to a cooler one obeys the first law of thermodynamics: energy is conserved.

Now consider the same process in reverse. Suppose that a hot frying pan in a sink of cold water were to become hotter while the water became cooler. As long as the same amount of thermal energy was gained by the frying pan and lost by the water, the first law of thermodynamics would be satisfied. Yet we all know that such a process cannot occur: heat always flows from a hot object to a cold one, never in the reverse direction. That is, by itself the magnitude of the heat flow associated with a process does not predict whether the process will occur spontaneously.

For many years, chemists and physicists tried to identify a single measurable quantity that would enable them to predict whether a particular process or reaction would occur spontaneously. Initially, many of them focused on enthalpy changes and hypothesized that an exothermic process would always be spontaneous. But although it is true that many, if not most, spontaneous processes are exothermic, there are also many spontaneous processes that are not exothermic. For example, at a pressure of 1 atm, ice melts spontaneously at temperatures greater than 0°C, yet this is an endothermic process because heat is absorbed. Similarly, many salts (such as NH_4NO_3, NaCl, and KBr) dissolve spontaneously in water even though they absorb heat from the surroundings as they dissolve (i.e., $\Delta H_{soln} > 0$). Reactions can also be both spontaneous and highly endothermic, like the reaction of barium hydroxide with ammonium thiocyanate shown in Figure $13.2.1$.

Figure $13.2.1$: An Endothermic Reaction. The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic, so water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes place in the flask freezes water that has been placed under the beaker, so the flask becomes frozen to the wood. For a full video: see www.youtube.com/watch?v=GQkJI-Nq3Os.

Thus enthalpy is not the only factor that determines whether a process is spontaneous. For example, after a cube of sugar has dissolved in a glass of water so that the sucrose molecules are uniformly dispersed in a dilute solution, they never spontaneously come back together in solution to form a sugar cube. Moreover, the molecules of a gas remain evenly distributed throughout the entire volume of a glass bulb and never spontaneously assemble in only one portion of the available volume. To help explain why these phenomena proceed spontaneously in only one direction requires an additional state function called entropy (S), a thermodynamic property of all substances that is proportional to their degree of disorder.

> The direction of a spontaneous process is not governed by the internal energy change nor enthalpy change and thus the First Law of Thermodynamics cannot predict the direction of a natural process

Probabilities and Microstates

Chemical and physical changes in a system may be accompanied by either an increase or a decrease in the disorder of the system, corresponding to an increase in entropy ($\Delta S > 0$) or a decrease in entropy ($\Delta S < 0$), respectively. As with any other state function, the change in entropy is defined as the difference between the entropies of the final and initial states:

$$\Delta S = S_f - S_i \tag{13.2.1}$$

When a gas expands into a vacuum, its entropy increases because the increased volume allows for greater atomic or molecular disorder. The greater the number of atoms or molecules in the gas, the greater the disorder. The magnitude of the entropy of a system depends on the number of microscopic states, or microstates, associated with it (in this case, the number of atoms or molecules); that is, the greater the number of microstates, the greater the entropy.

How can we express disorder quantitatively? From the example of coins, you can probably see that simple statistics plays a role: the probability of obtaining three heads and seven tails after tossing ten coins is just the ratio of the number of ways that ten different coins can be arranged in this way, to the number of all possible arrangements of ten coins.

Using the language of molecular statistics, we say that a collection of coins in which a given fraction of its members are heads-up constitutes a *macroscopic state* of the system. Since we do not care which coins are heads-up, there are clearly numerous configurations of the individual coins which can result in this "macrostate". Each of these configurations specifies a *microscopic state* of the system. The greater the number of microstates that correspond to a given macrostate (or configuration), the greater the probability of that macrostate. To see what this means, consider the possible outcomes of a toss of four coins (Table $13.2.1$):

Table 13.2.1: Coin Toss Results

macrostate (Configuration)	ways	probability	microstates
0 heads	1	1/16	TTTT
1 head	4	4/16 = 1/4	HTTT THTT TTHT TTTH
2 heads	6	6/16 = 3/8	HHTT HTHT HTTH THHT TTHH THTH
3 heads	4	4/16 = 1/4	HHHT HTHH HHTH THHH
4 heads	1	1/16	HHHH

A toss of four coins will yield one of the five outcomes (macrostates) listed in the leftmost column of the table. The second column gives the number of "ways"— that is, the number of head/tail configurations of the set of coins (the number of microstates)— that can result in the macrostate. The probability of a toss resulting in a particular macrostate is proportional to the number of microstates corresponding to the macrostate, and is equal to this number, divided by the total number of possible microstates (in this example, 2^4 =16). An important assumption here is that all microstates are equally probable; that is, the toss is a "fair" one in which the many factors that determine the trajectory of each coin operate in an entirely random way.

> The greater the number of **microstates** that correspond to a given **macrostate**, the greater the probability of that **macrostate**.

Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the number of *microstates* possible for the system. A microstate (Ω) is a specific configuration of the locations and energies of the atoms or molecules that comprise a system like the following:

$$S = k \ln \Omega \tag{13.2.2}$$

Here *k* is the Boltzmann constant and has a value of 1.38 × 10^{-23} J/K.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\begin{aligned} \Delta S &= S_\text{f} - S_\text{i} && (13.2.3)\\ &= k \ln \Omega_\text{f} - k \ln \Omega_\text{i} && (13.2.4)\\ &= k \ln \frac{\Omega_\text{f}}{\Omega_\text{i}} && (13.2.5) \end{aligned}$$

For processes involving an increase in the number of microstates, $\Omega_f > \Omega_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $\Omega_f < \Omega_i$, yield a decrease in system entropy, $\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

Consider the general case of a system comprised of *N* particles distributed among *n* boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in 2^4 = 16 different microstates as illustrated in Figure 13.2.2. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates (Equation 13.2.2), *the most probable distribution is therefore the one of greatest entropy*.

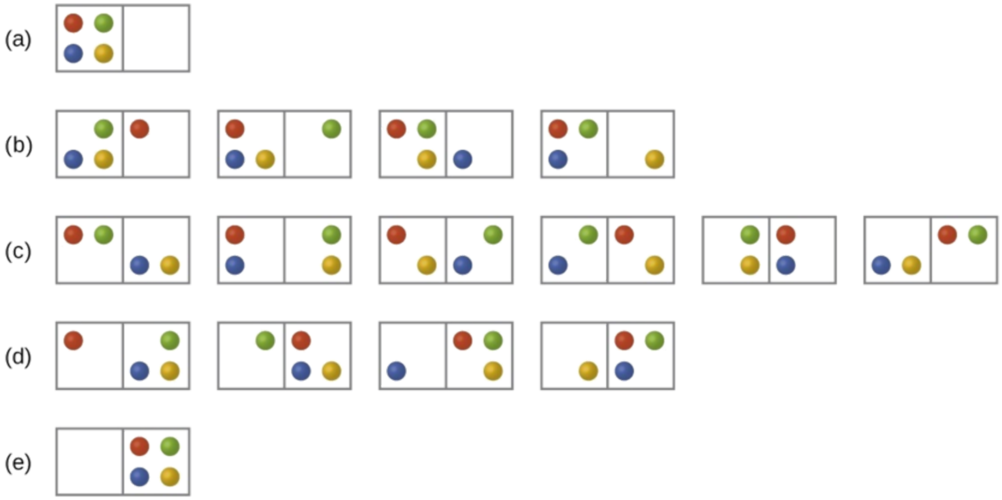


Figure 13.2.2: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is

$$\frac{6}{16} = \frac{3}{8}$$

The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of

$$\frac{1}{16}$$

The probability of finding all particles in only one box (either the left box or right box) is then

$$\left(\frac{1}{16}+\frac{1}{16}\right)=\frac{2}{16}=\frac{1}{8}$$

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

The previous description of an ideal gas expanding into a vacuum is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. The spontaneous process whereby the gas contained initially in one flask expands to fill both flasks equally therefore yields an increase in entropy for the system.

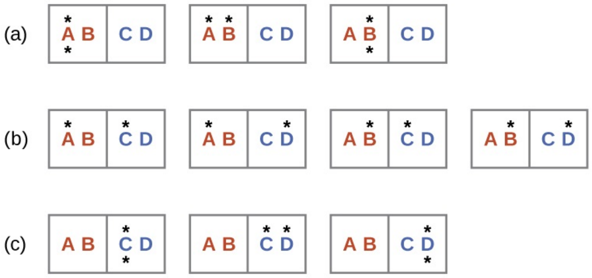
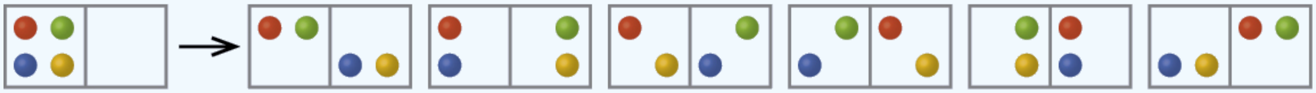


Figure 13.2.3: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles A and B contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of energy (represented as "*") in Figure 13.2.3. The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. And so, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. As for the previous example of matter dispersal, extrapolating this treatment to macroscopic collections of particles dramatically increases the probability of the uniform distribution relative to the other distributions. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects' temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

✓ Example 13.2.1: Determination of ΔS

Consider the system shown here. What is the change in entropy for a process that converts the system from distribution (a) to (c)?



Solution

We are interested in the following change:

The initial number of microstates is one, the final six:

$$\begin{aligned}\Delta S &= k \ln \frac{\Omega_c}{\Omega_a} \\ &= 1.38 \times 10^{-23}\ J/K \times \ln \frac{6}{1} \\ &= 2.47 \times 10^{-23}\ J/K\end{aligned}$$

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

? Exercise 13.2.1

Consider the system shown in Figure 13.2.3. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer

0 J/K

A disordered system has a greater number of possible microstates than does an ordered system, so it has a higher entropy. This is most clearly seen in the entropy changes that accompany phase transitions, such as solid to liquid or liquid to gas. As you know, a crystalline solid is composed of an ordered array of molecules, ions, or atoms that occupy fixed positions in a lattice, whereas the molecules in a liquid are free to move and tumble within the volume of the liquid; molecules in a gas have even more freedom to move than those in a liquid. Each degree of motion increases the number of available microstates, resulting in a higher entropy. Thus the entropy of a system must increase during melting ($\Delta S_{fus} > 0$). Similarly, when a liquid is converted to a vapor, the greater freedom of motion of the molecules in the gas phase means that $\Delta S_{vap} > 0$. Conversely, the reverse processes (condensing a vapor to form a liquid or freezing a liquid to form a solid) must be accompanied by a decrease in the entropy of the system: $\Delta S < 0$.

Definition: Entropy

Entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. The greater the number of possible microstates for a system, the greater the disorder and the higher the entropy.

Disorder is more probable than order because there are so many more ways of achieving it. Thus coins and cards tend to assume random configurations when tossed or shuffled, and socks and books tend to become more scattered about a teenager's room during the course of daily living. But there are some important differences between these large-scale mechanical, or macro systems, and the collections of sub-microscopic particles that constitute the stuff of chemistry, and which we will refer to here generically as **molecules**. Molecules, unlike macro objects, are capable of accepting, storing, and giving up energy in tiny amounts (quanta), and act as highly efficient carriers and spreaders of thermal energy as they move around. Thus, **in chemical systems**,

1. **We are dealing with huge numbers of particles**. This is important because statistical predictions are always more accurate for larger samples. Thus although for the four tosses there is a good chance (62%) that the H/T ratio will fall outside the range of 0.45 - 0.55, this probability becomes almost zero for 1000 tosses. To express this in a different way, the chances that 1000 gas molecules moving about randomly in a container would at any instant be distributed in a sufficiently non-uniform manner to produce a detectable pressure difference between the two halves of a container will be extremely small. If we increase the number of molecules to a chemically significant number (around 10^{20}, say), then the same probability becomes indistinguishable from zero.
2. **Once the change begins, it proceeds spontaneously.** That is, no external agent (a tosser, shuffler, or teenager) is needed to keep the process going. Gases will spontaneously expand if they are allowed to, and reactions, once started, will proceed toward equilibrium.
3. **Thermal energy is continually being exchanged between the particles of the system, and between the system and the surroundings.** Collisions between molecules result in exchanges of momentum (and thus of kinetic energy) amongst the particles of the system, and (through collisions with the walls of a container, for example) with the surroundings.

4. **Thermal energy spreads rapidly and randomly throughout the various energetically accessible microstates of the system.** The **direction** of spontaneous change is that which results in the maximum possible spreading and sharing of thermal energy.

The importance of these last two points is far greater than you might at first think, but to fully appreciate this, you must recall the various ways in which thermal energy is stored in molecules.

Sign of Entropy Change

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure $13.2.4$ In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{liquid} > S_{solid}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

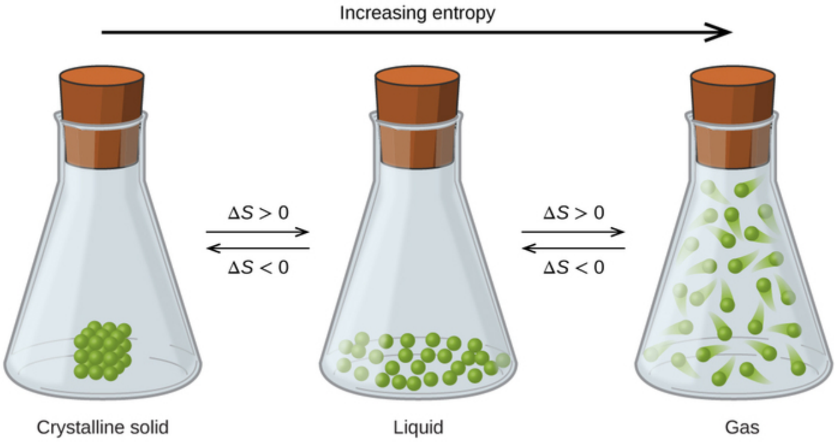


Figure 13.2.4: The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the vapor or gas phase. The atoms or molecules occupy a *much* greater volume than in the liquid phase; therefore each atom or molecule can be found in many more locations than in the liquid (or solid) phase. Consequently, for any substance,

$$S_{gas} \gg S_{liquid} > S_{solid} \tag{13.2.6}$$

and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure $13.2.5$).

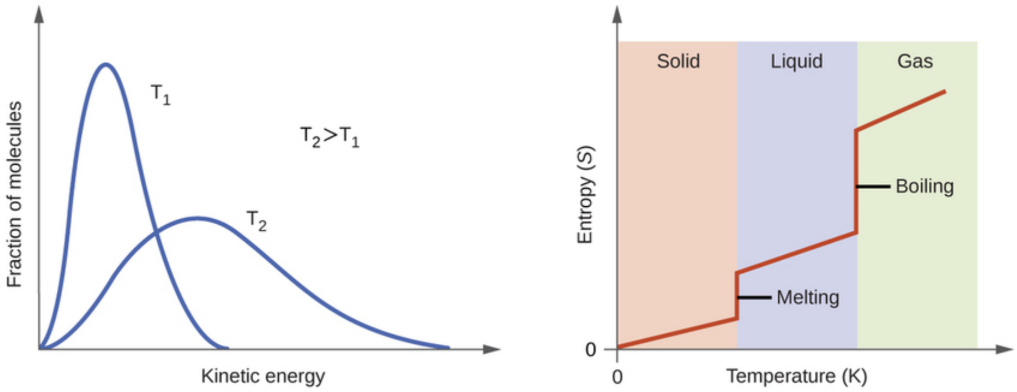


Figure 13.2.5: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

The entropy of a substance is influenced by structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (which is a topic beyond the scope of our treatment). For molecules, greater numbers of atoms (regardless of their masses) increase the ways in which the molecules can vibrate and thus the number of possible microstates and the system entropy.

Finally, variations in the types of particles affect the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in Example $13.2.2$

✓ Example 13.2.2: Predicting the Sign of ΔS

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

a. One mole liquid water at room temperature ⟶ one mole liquid water at 50 °C
b. $\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \longrightarrow \mathrm{AgCl}(s)$
c. $\mathrm{C_6H_6(l)} + \frac{15}{2}\mathrm{O_2(g)} \longrightarrow 6\,\mathrm{CO_2(g)} + 3\,\mathrm{H_2O(l)}$
d. $\mathrm{NH_3}(s) \longrightarrow \mathrm{NH_3}(l)$

Solution

a. positive, temperature increases
b. negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter
c. negative, net decrease in the amount of gaseous species
d. positive, phase transition from solid to liquid, net increase in dispersal of matter

? Exercise 13.2.2

Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

a. $\mathrm{NaNO_3}(s) \longrightarrow \mathrm{Na^+}(aq) + \mathrm{NO_3^-}(aq)$
b. the freezing of liquid water
c. $\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g)$
d. $\mathrm{CaCO}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$

Answer a

Positive; The solid dissolves to give an increase of mobile ions in solution.

Answer b

Negative; The liquid becomes a more ordered solid.

Answer c

Positive; The relatively ordered solid becomes a gas.

Answer d

Positive; There is a net production of one mole of gas.

Summary

Entropy (S) is a state function that can be related to the number of microstates for a system (the number of ways the system can be arranged) and to the ratio of reversible heat to kelvin temperature. It may be interpreted as a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the "disorder" of the system. For a given substance, $S_{solid} < S_{liquid} \ll S_{gas}$ in a given physical state at a given temperature, entropy is typically greater for heavier atoms or more complex molecules. Entropy increases when a system is heated and when solutions form. Using these guidelines, the sign of entropy changes for some chemical reactions may be reliably predicted.

Contributors and Attributions

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13.3: Entropy and Heat - Experimental Basis of the Second Law of Thermodynamics

Learning Objectives

- The Learning Objective of this Module is to understand the relationship between internal energy and entropy.

Thermodynamic Definition of Entropy

Experiments show that the magnitude of ΔS_{vap} is 80–90 J/(mol•K) for a wide variety of liquids with different boiling points. However, liquids that have highly ordered structures due to hydrogen bonding or other intermolecular interactions tend to have significantly higher values of ΔS_{vap}. For instance, ΔS_{vap} for water is 102 J/(mol•K). Another process that is accompanied by entropy changes is the formation of a solution. As illustrated in Figure 13.3.1, the formation of a liquid solution from a crystalline solid (the solute) and a liquid solvent is expected to result in an increase in the number of available microstates of the system and hence its entropy. Indeed, dissolving a substance such as NaCl in water disrupts both the ordered crystal lattice of $NaCl$ and the ordered hydrogen-bonded structure of water, leading to an increase in the entropy of the system. At the same time, however, each dissolved Na^+ ion becomes hydrated by an ordered arrangement of at least six water molecules, and the $Cl^−$ ions also cause the water to adopt a particular local structure. Both of these effects increase the order of the system, leading to a decrease in entropy. The overall entropy change for the formation of a solution therefore depends on the relative magnitudes of these opposing factors. In the case of an $NaCl$ solution, disruption of the crystalline $NaCl$ structure and the hydrogen-bonded interactions in water is quantitatively more important, so $\Delta S_{soln} > 0$.

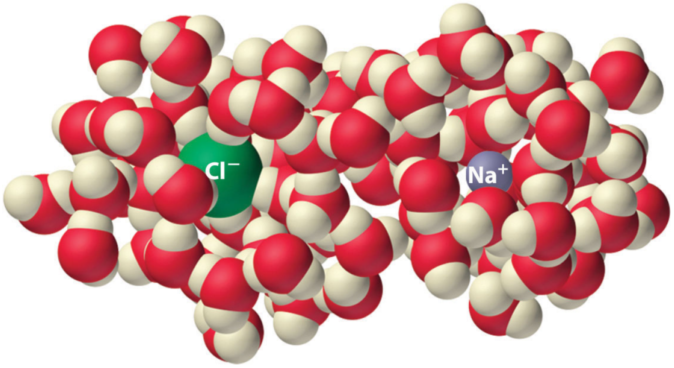


Figure 13.3.1: The Effect of Solution Formation on Entropy

Dissolving $NaCl$ in water results in an increase in the entropy of the system. Each hydrated ion, however, forms an ordered arrangement with water molecules, which decreases the entropy of the system. The magnitude of the increase is greater than the magnitude of the decrease, so the overall entropy change for the formation of an NaCl solution is positive.

Example 13.3.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of $NH_3(g)$ or 1 mol of He(g), both at 25°C
b. 1 mol of Pb(s) at 25°C or 1 mol of Pb(l) at 800°C

Given: amounts of substances and temperature

Asked for: higher entropy

Strategy:

From the number of atoms present and the phase of each substance, predict which has the greater number of available microstates and hence the higher entropy.

Solution:

a. Both substances are gases at 25°C, but one consists of He atoms and the other consists of NH_3 molecules. With four atoms instead of one, the NH_3 molecules have more motions available, leading to a greater number of microstates. Hence we predict that the NH_3 sample will have the higher entropy.

b. The nature of the atomic species is the same in both cases, but the phase is different: one sample is a solid, and one is a liquid. Based on the greater freedom of motion available to atoms in a liquid, we predict that the liquid sample will have the higher entropy.

? Exercise 13.3.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of He(g) at 10 K and 1 atm pressure or 1 mol of He(g) at 250°C and 0.2 atm
b. a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm or a sample of 2 mol of $NH_3(g)$ at 25°C and 1 atm

Answer a

1 mol of He(g) at 250°C and 0.2 atm (higher temperature and lower pressure indicate greater volume and more microstates)

Answer b

a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm (more molecules of gas are present)

Video Solution

Summary

A reversible process is one for which all intermediate states between extremes are equilibrium states; it can change direction at any time. In contrast, an irreversible process occurs in one direction only. The change in entropy of the system or the surroundings is the quantity of heat transferred divided by the temperature. The second law of thermodynamics states that in a reversible process, the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.

13.4: Entropy Changes in Reversible Processes

Learning Objectives

You are expected to be able to define and explain the significance of terms identified in ***bold***.

- A ***reversible*** *process* is one carried out in infinitesimal steps after which, when undone, both the system and surroundings (that is, the world) remain unchanged (see the example of gas expansion-compression below). Although true reversible change cannot be realized in practice, it can always be approximated.
- As a process is carried out in a more reversible manner, the value of w approaches its maximum possible value, and q approaches its minimum possible value.
- Although q is not a state function, the quotient q_{rev}/T is, and is known as the *entropy*.

A change is said to occur reversibly when it can be carried out in a series of infinitesimal steps, each one of which can be undone by making a similarly minute change to the conditions that bring the change about. For example, the reversible expansion of a gas can be achieved by reducing the external pressure in a series of infinitesimal steps; reversing any step will restore the system and the surroundings to their previous state. Similarly, heat can be transferred reversibly between two bodies by changing the temperature difference between them in infinitesimal steps each of which can be undone by reversing the temperature difference.

The most widely cited example of an **irreversible** change is the free expansion of a gas into a vacuum. Although the system can always be restored to its original state by recompressing the gas, this would require that the surroundings perform work on the gas. Since the gas does no work on the surrounding in a free expansion (the external pressure is zero, so $P\Delta V = 0$,) there will be a permanent change in the surroundings. Another example of irreversible change is the conversion of mechanical work into frictional heat; there is no way, by reversing the motion of a weight along a surface, that the heat released due to friction can be restored to the system.

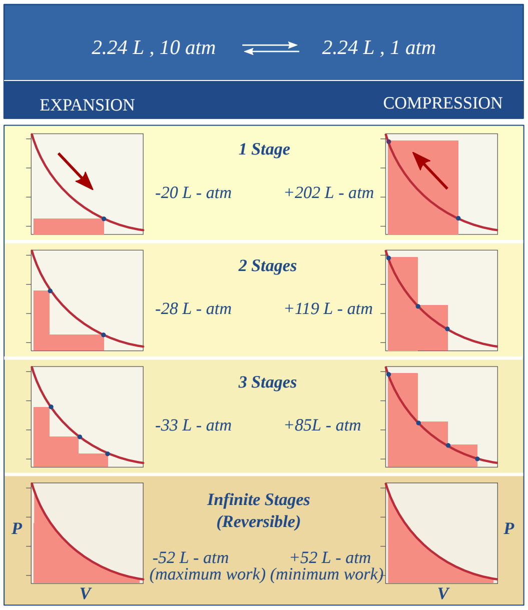


Figure 13.4.1: Reversible vs. Irreversible Expansions and Compressions. (CC BY-NC; Ümit Kaya)

These diagrams show the same expansion and compression $\pm\Delta V$ carried out in different numbers of steps ranging from a single step at the top to an "infinite" number of steps at the bottom. As the number of steps increases, the processes become less irreversible; that is, the difference between the work done in expansion and that required to re-compress the gas diminishes. In the limit of an ”infinite” number of steps (bottom), these work terms are identical, and both the system and surroundings (the “world”) are unchanged by the expansion-compression cycle. In all other cases the system (the gas) is restored to its initial state, **but the *surroundings* are forever changed.**

Definition: Reversible Changes

A reversible change is one carried out in such as way that, when undone, both the system and surroundings (that is, the world) remain unchanged.

It should go without saying, of course, that any process that proceeds in infinitesimal steps would take infinitely long to occur, so thermodynamic reversibility is an idealization that is never achieved in real processes, except when the system is already at equilibrium, in which case no change will occur anyway! So why is the concept of a reversible process so important?

The answer can be seen by recalling that the change in the internal energy that characterizes any process can be distributed in an infinity of ways between heat flow across the boundaries of the system and work done on or by the system, as expressed by the First Law of thermodynamics

$$\Delta U = q + w. \tag{13.4.1}$$

Each combination of q and w represents a different pathway between the initial and final states. It can be shown that as a process such as the expansion of a gas is carried out in successively longer series of smaller steps, the absolute value of q approaches a minimum, and that of w approaches a maximum that is characteristic of the particular process. Thus when a process is carried out reversibly, the w-term in Equation 13.4.1 has its greatest possible value, and the q-term is at its smallest. These special quantities w_{max} and q_{min} (which we denote as q_{rev} and pronounce “q-reversible”) have unique values for any given process and are therefore state functions.

Work and Reversibility

Changes in entropy (ΔS), together with changes in enthalpy (ΔH), enable us to predict in which direction a chemical or physical change will occur spontaneously. Before discussing how to do so, however, we must understand the difference between a reversible process and an irreversible one. In a reversible process, every intermediate state between the extremes is an equilibrium state, regardless of the direction of the change. In contrast, an irreversible process is one in which the intermediate states are not equilibrium states, so change occurs spontaneously in only one direction. As a result, a reversible process can change direction at any time, whereas an irreversible process cannot. When a gas expands reversibly against an external pressure such as a piston, for example, the expansion can be reversed at any time by reversing the motion of the piston; once the gas is compressed, it can be allowed to expand again, and the process can continue indefinitely. In contrast, the expansion of a gas into a vacuum ($P_{ext} = 0$) is irreversible because the external pressure is measurably less than the internal pressure of the gas. No equilibrium states exist, and the gas expands irreversibly. When gas escapes from a microscopic hole in a balloon into a vacuum, for example, the process is irreversible; the direction of airflow cannot change.

Because work done during the expansion of a gas depends on the opposing external pressure ($w = P_{ext}\Delta V$), work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$. Whether a process is reversible or irreversible, the first law of thermodynamics holds (Equation 13.4.1). Because U is a state function, the magnitude of ΔU does not depend on reversibility and is independent of the path taken. So

$$\Delta U = q_{rev} + w_{rev} \tag{13.4.2}$$

$$= q_{irrev} + w_{irrev} \tag{13.4.3}$$

Work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process:

$$w_{rev} \geq w_{irrev} \tag{13.4.4}$$

In other words, ΔU for a process is the same whether that process is carried out in a reversible manner or an irreversible one. We now return to our earlier definition of entropy, using the magnitude of the heat flow for a reversible process (q_{rev}) to define entropy quantitatively.

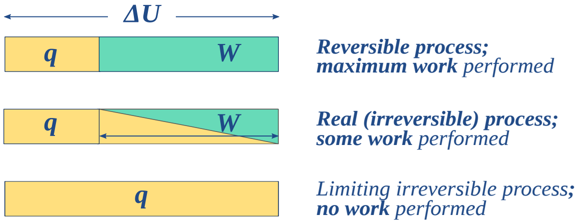


Figure 13.4.2: Note that the reversible condition implies w_{max} and q_{min}. The impossibility of extracting all of the internal energy as work is essentially a statement of the Second Law. (CC BY-NC; Ümit Kaya)

For a process that reversibly exchanges a quantity of heat q_{rev} with the surroundings, the entropy change is defined as

$$\Delta S = \frac{q_{rev}}{T} \tag{13.4.5}$$

This is the basic way of evaluating ΔS for *constant-temperature processes* such as phase changes, or the isothermal expansion of a gas. For processes in which the temperature is not constant such as heating or cooling of a substance, the equation must be integrated over the required temperature range, as discussed below.

Q&A: If no real process can take place reversibly, what use is an expression involving q_{rev}?

This is a rather fine point that you should understand: although transfer of heat between the system and surroundings is impossible to achieve in a truly reversible manner, this idealized pathway is only crucial for the definition of ΔS; by virtue of its being a state function, the same value of ΔS will apply when the system undergoes the same net change via any pathway. For example, the entropy change a gas undergoes when its volume is doubled at constant temperature will be the same regardless of whether the expansion is carried out in 1000 tiny steps (as reversible as patience is likely to allow) or by a single-step (as irreversible a pathway as you can get!) expansion into a vacuum (Figure $13.4.1$).

Entropy is an *extensive* quantity; that is, it is proportional to the quantity of matter in a system; thus 100 g of metallic copper has twice the entropy of 50 g at the same temperature. This makes sense because the larger piece of copper contains twice as many quantized energy levels able to contain the thermal energy.

Entropy and "disorder"

Entropy is still described, particularly in older textbooks, as a measure of disorder. In a narrow technical sense this is correct, since the spreading and sharing of thermal energy does have the effect of randomizing the disposition of thermal energy within a system. But to simply equate entropy with “disorder” without further qualification is extremely misleading because it is far too easy to forget that entropy (and thermodynamics in general) applies only to molecular-level systems capable of exchanging thermal energy with the surroundings. Carrying these concepts over to macro systems may yield compelling analogies, but it is no longer science. It is far better to avoid the term “disorder” altogether in discussing entropy.

ΔS_{sys} for an Isothermal Expansion (or Compression)

As a substance becomes more dispersed in space, the thermal energy it carries is also spread over a larger volume, leading to an increase in its entropy. Because entropy, like energy, is an extensive property, a dilute solution of a given substance may well possess a smaller entropy than the same volume of a more concentrated solution, but the entropy *per mole* of solute (the *molar* entropy) will of course always increase as the solution becomes more dilute.

For gaseous substances, the volume and pressure are respectively direct and inverse measures of concentration. For an ideal gas that expands at a constant temperature (meaning that it absorbs heat from the surroundings to compensate for the work it does during the expansion), the increase in entropy is given by

$$\Delta S = R\ln\left(\frac{V_2}{V_1}\right) \tag{13.4.6}$$

Note: If the gas is allowed to cool during the expansion, the relation becomes more complicated and will best be discussed in a more advanced course.

Because the pressure of an ideal gas is *inversely proportional* to its volume, i.e.,

$$P = \frac{nRT}{V} \tag{13.4.7}$$

we can easily alter Equation 13.4.6to express the entropy change associated with a change in the pressure of an ideal gas:

$$\Delta S = R\ln\left(\frac{P_1}{P_2}\right) \tag{13.4.8}$$

Also the concentration $c = n/V$ for an ideal gas is *proportional* to pressure

$$P = cRT \tag{13.4.9}$$

we can expressing the entropy change directly in concentrations, we have the similar relation

$$\Delta S = R\ln\left(\frac{c_1}{c_2}\right) \tag{13.4.10}$$

Although these equations strictly apply only to perfect gases and cannot be used at all for liquids and solids, it turns out that in a dilute solution, the solute can often be treated as a gas dispersed in the volume of the solution, so the last equation can actually give a fairly accurate value for the entropy of dilution of a solution. We will see later that this has important consequences in determining the equilibrium concentrations in a homogeneous reaction mixture.

The Relationship between Internal Energy and Entropy

Because the quantity of heat transferred (q_{rev}) is directly proportional to the absolute temperature of an object (T) ($q_{rev} \propto T$), the hotter the object, the greater the amount of heat transferred. Moreover, adding heat to a system increases the kinetic energy of the component atoms and molecules and hence their disorder ($\Delta S \propto q_{rev}$). Combining these relationships for any reversible process,

$$q_{\text{rev}} = T\Delta S \tag{13.4.11}$$

and

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{13.4.12}$$

Because the numerator (q_{rev}) is expressed in units of energy (joules), the units of ΔS are joules/kelvin (J/K). Recognizing that the work done in a reversible process at constant pressure is

$$w_{rev} = -P\Delta V, \tag{13.4.13}$$

we can express Equation 13.4.3as follows:

$$\Delta U = q_{rev} + w_{rev} \tag{13.4.14}$$

$$= T\Delta S - P\Delta V \tag{13.4.15}$$

Thus the change in the internal energy of the system is related to the change in entropy, the absolute temperature, and the PV work done.

To illustrate the use of Equation 13.4.12 and Equation 13.4.15, we consider two reversible processes before turning to an irreversible process. When a sample of an ideal gas is allowed to expand reversibly at constant temperature, heat must be added to the gas during expansion to keep its T constant (Figure 13.4.5). The internal energy of the gas does not change because the temperature of the gas does not change; that is, $\Delta U = 0$ and $q_{rev} = -w_{rev}$. During expansion, $\Delta V > 0$, so the gas performs work on its surroundings:

$$w_{rev} = -P\Delta V < 0. \tag{13.4.16}$$

According to Equation 13.4.15, this means that q_{rev} must increase during expansion; that is, the gas must absorb heat from the surroundings during expansion, and the surroundings must give up that same amount of heat. The entropy change of the *system* is therefore

$$\Delta S_{sys} = +\frac{q_{rev}}{T} \tag{13.4.17}$$

and the entropy change of the *surroundings* is

$$\Delta S_{surr} = -\frac{q_{rev}}{T}. \tag{13.4.18}$$

The corresponding change in entropy of the universe is then as follows:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{13.4.19}$$

$$= \frac{q_{\text{rev}}}{T} + \left(-\frac{q_{\text{rev}}}{T}\right) \tag{13.4.20}$$

$$= 0 \tag{13.4.21}$$

Thus no change in ΔS_{univ} has occurred.

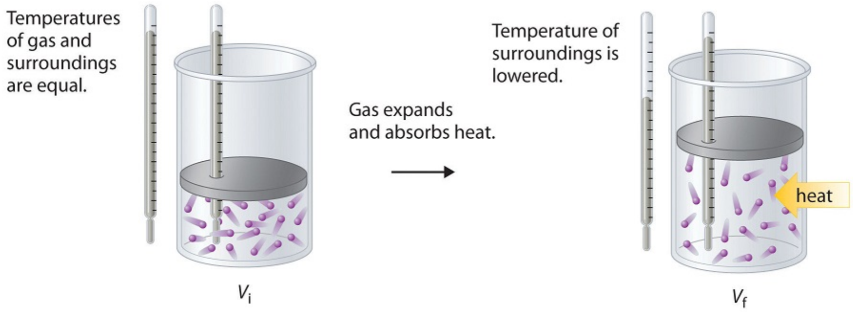


Figure 13.4.5: Expansion of Gas at Constant Temperature. (CC BY-SA-NC; Anonymous by request)

In the initial state (top), the temperatures of a gas and the surroundings are the same. During the reversible expansion of the gas, heat must be added to the gas to maintain a constant temperature. Thus the internal energy of the gas does not change, but work is performed on the surroundings. In the final state (bottom), the temperature of the surroundings is lower because the gas has absorbed heat from the surroundings during expansion.

Now consider the reversible melting of a sample of ice at 0°C and 1 atm. The enthalpy of fusion of ice is 6.01 kJ/mol, which means that 6.01 kJ of heat are absorbed reversibly from the surroundings when 1 mol of ice melts at 0°C, as illustrated in Figure 13.4.6. The surroundings constitute a sample of low-density carbon foam that is thermally conductive, and the system is the ice cube that has been placed on it. The direction of heat flow along the resulting temperature gradient is indicated with an arrow. From Equation 13.4.12, we see that the entropy of fusion of ice can be written as follows:

$$\Delta S_{\text{fus}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{fus}}}{T} \tag{13.4.22}$$

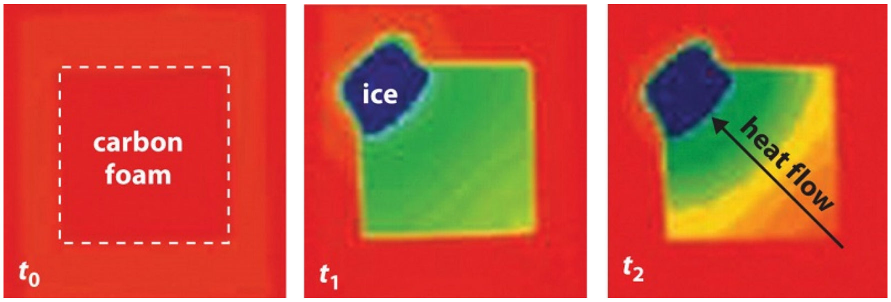


Figure 13.4.6: Thermograms Showing That Heat Is Absorbed from the Surroundings When Ice Melts at 0°C

By convention, a thermogram shows cold regions in blue, warm regions in red, and thermally intermediate regions in green. When an ice cube (the system, dark blue) is placed on the corner of a square sample of low-density carbon foam with very high thermal conductivity, the temperature of the foam is lowered (going from red to green). As the ice melts, a temperature gradient appears, ranging from warm to very cold. An arrow indicates the direction of heat flow from the surroundings (red and green) to the ice cube. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so the entropy of the universe does not change.

In this case,

$$\begin{aligned} \Delta S_{fus} &= \frac{6.01\ kJ/mol}{273\ K} && (13.4.23)\\ &= 22.0\ J/(mol \bullet K) && (13.4.24)\\ &= \Delta S_{sys}. && (13.4.25) \end{aligned}$$

The amount of heat lost by the surroundings is the same as the amount gained by the ice, so

$$\begin{aligned} \Delta S_{surr} &= \frac{q_{rev}}{T} && (13.4.26)\\ &= \frac{-6.01\ kJ/mol}{273\ K} && (13.4.27)\\ &= -22.0\ J/(mol \bullet K). && (13.4.28) \end{aligned}$$

Once again, we see that the entropy of the universe does not change:

$$\begin{aligned} \Delta S_{univ} &= \Delta S_{sys} + \Delta S_{surr} && (13.4.29)\\ &= 22.0\ J/(mol \bullet K) - 22.0\ J/(mol \bullet K) && (13.4.30)\\ &= 0 && (13.4.31) \end{aligned}$$

In these two examples of reversible processes, the entropy of the universe is unchanged. This is true of all reversible processes and constitutes part of the second law of thermodynamics: the entropy of the universe remains constant in a reversible process, whereas the entropy of the universe increases in an irreversible (spontaneous) process.

The Second Law of Thermodynamics

The entropy of the universe **increases** during a spontaneous process. It also **increases** during an observable non-spontaneous process.

As an example of an irreversible process, consider the entropy changes that accompany the spontaneous and irreversible transfer of heat from a hot object to a cold one, as occurs when lava spewed from a volcano flows into cold ocean water. The cold substance, the water, gains heat ($q > 0$), so the change in the entropy of the water can be written as $\Delta S_{cold} = q/T_{cold}$. Similarly, the hot substance, the lava, loses heat ($q < 0$), so its entropy change can be written as $\Delta S_{hot} = -q/T_{hot}$, where T_{cold} and T_{hot} are the temperatures of the cold and hot substances, respectively. The total entropy change of the universe accompanying this process is therefore

$$\Delta S_{\text{univ}} = \Delta S_{\text{cold}} + \Delta S_{\text{hot}} \tag{13.4.32}$$

$$= \frac{q}{T_{\text{cold}}} + \left(-\frac{q}{T_{\text{hot}}}\right) \tag{13.4.33}$$

The numerators on the right side of Equation 13.4.33 are the same in magnitude but opposite in sign. Whether $ΔS_{univ}$ is positive or negative depends on the relative magnitudes of the denominators. By definition, $T_{hot} > T_{cold}$, so $−q/T_{hot}$ must be less than q/T_{cold}, and $ΔS_{univ}$ must be positive. As predicted by the second law of thermodynamics, the entropy of the universe increases during this irreversible process. Any process for which $ΔS_{univ}$ is positive is, by definition, a spontaneous one that will occur as written. Conversely, any process for which $ΔS_{univ}$ approaches zero will not occur spontaneously as written but will occur spontaneously in the reverse direction. We see, therefore, that heat is spontaneously transferred from a hot substance, the lava, to a cold substance, the ocean water. In fact, if the lava is hot enough (e.g., if it is molten), so much heat can be transferred that the water is converted to steam (Figure 13.4.7).

Figure 13.4.7: Spontaneous Transfer of Heat from a Hot Substance to a Cold Substance

When molten lava flows into cold ocean water, so much heat is spontaneously transferred to the water that steam is produced.

Example 13.4.1: Tin Pest

Tin has two allotropes with different structures. Gray tin (α-tin) has a structure similar to that of diamond, whereas white tin (β-tin) is denser, with a unit cell structure that is based on a rectangular prism. At temperatures greater than 13.2°C, white tin is the more stable phase, but below that temperature, it slowly converts reversibly to the less dense, powdery gray phase. This phenomenon was argued to plagued Napoleon’s army during his ill-fated invasion of Russia in 1812: the buttons on his soldiers’ uniforms were made of tin and disintegrated during the Russian winter, adversely affecting the soldiers’ health (and morale). The conversion of white tin to gray tin is exothermic, with ΔH = −2.1 kJ/mol at 13.2°C.

a. What is ΔS for this process?
b. Which is the more highly ordered form of tin—white or gray?

Given: ΔH and temperature

Asked for: ΔS and relative degree of order

Strategy:

Use Equation 13.4.12 to calculate the change in entropy for the reversible phase transition. From the calculated value of ΔS, predict which allotrope has the more highly ordered structure.

Solution

a. We know from Equation 13.4.12 that the entropy change for any reversible process is the heat transferred (in joules) divided by the temperature at which the process occurs. Because the conversion occurs at constant pressure, and ΔH and ΔU are essentially equal for reactions that involve only solids, we can calculate the change in entropy for the reversible phase transition where q_{rev} = ΔH. Substituting the given values for ΔH and temperature in kelvins (in this case, T = 13.2°C = 286.4 K),

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{(-2.1\ \text{kJ/mol})(1000\ \text{J/kJ})}{286.4\ \text{K}} = -7.3\ \text{J/(mol}\cdot\text{K)}$$

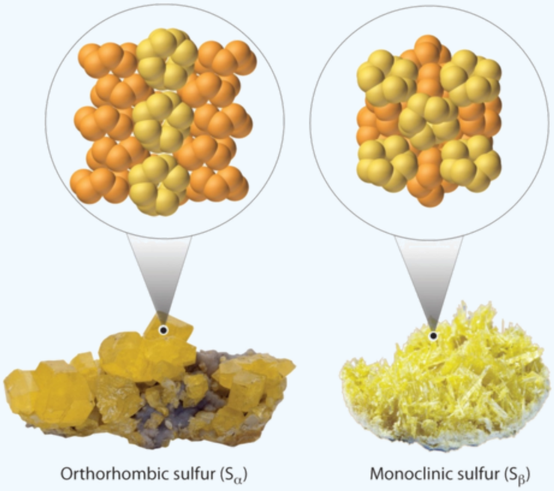
b. The fact that $\Delta S < 0$ means that entropy decreases when white tin is converted to gray tin. Thus gray tin must be the more highly ordered structure.

Video 13.4.1: Time lapse tin pest reaction. Beta tin to alpha tin transformation, time lapse video of sample maintained at -40 C. 20 shots per hour.

Note: Whether failing buttons were indeed a contributing factor in the failure of the invasion remains disputed; critics of the theory point out that the tin used would have been quite impure and thus more tolerant of low temperatures. Laboratory tests provide evidence that the time required for unalloyed tin to develop significant tin pest damage at lowered temperatures is about 18 months, which is more than twice the length of Napoleon's Russian campaign. It is clear though that some of the regiments employed in the campaign had tin buttons and that the temperature reached sufficiently low values (at least -40 °C) to facilitate tin pest.

? Exercise 13.4.1: Sulfur

Elemental sulfur exists in two forms: an orthorhombic form (S_α), which is stable below 95.3°C, and a monoclinic form (S_β), which is stable above 95.3°C. The conversion of orthorhombic sulfur to monoclinic sulfur is endothermic, with $\Delta H = 0.401\ kJ/mol$ at 1 atm.



a. What is ΔS for this process?
b. Which is the more highly ordered form of sulfur—S_α or S_β?

Answer a

1.09 J/(mol•K)

Answer b

S_α

Summary

During a spontaneous process, the entropy of the universe increases.

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

A reversible process is one for which all intermediate states between extremes are *equilibrium states*; it can change direction at any time. In contrast, an irreversible process occurs in one direction only. The change in entropy of the system or the surroundings is the quantity of heat transferred divided by the temperature. The second law of thermodynamics states that in a reversible process, the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.

13.5: Entropy Changes and Spontaneity

Learning Objectives

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

Connecting Entropy and Heat to Spontaneity

In the quest to identify a property that may reliably predict the spontaneity of a process, we have identified a very promising candidate: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S_{sys} > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{13.5.1}$$

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

   $$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \tag{13.5.2}$$

   and

   $$\Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}} \tag{13.5.3}$$

   The arithmetic signs of q_{rev} denote the loss of heat by the system and the gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the magnitude of the entropy change for the surroundings will be greater than that for the system, and so the sum of ΔS_{sys} and ΔS_{surr} will yield a positive value for ΔS_{univ}. *This process involves an increase in the entropy of the universe.*
2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

   $$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \tag{13.5.4}$$

   and

   $$\Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}} \tag{13.5.5}$$

   The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*
3. The temperature difference between the objects is infinitesimally small, $T_{sys} \approx T_{surr}$, and so the heat flow is thermodynamically *reversible*. See the previous section's discussion). In this case, the system and surroundings experience entropy changes that are equal in magnitude and therefore sum to yield a value of zero for ΔS_{univ}. *This process involves no change in the entropy of the universe.*

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the second law of thermodynamics: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in Table $13.5.1$.

Table 13.5.1: The Second Law of Thermodynamics

$\Delta S_{univ} > 0$	spontaneous

$\Delta S_{univ} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{univ} = 0$	reversible (system is at equilibrium)

Definition: The Second Law of Thermodynamics

All spontaneous changes cause an increase in the entropy of the universe, i.e.,

$$\Delta S_{\text{univ}} > 0. \tag{13.5.6}$$

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev}, and the second law may be stated as the following:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{13.5.7}$$

$$= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \tag{13.5.8}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example $13.5.1$.

Example 13.5.1: Will Ice Spontaneously Melt?

The entropy change for the process

$$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$$

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at −10.00 °C? Is it spontaneous at +10.00 °C?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = −6.00 kJ.

At −10.00 °C (263.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\ \text{J/K} + \frac{-6.00 \times 10^3\ \text{J}}{263.15\ \text{K}} \\ &= -0.7\ J/K\end{aligned}$$

$S_{\text{univ}} < 0$, so melting is nonspontaneous (*not* spontaneous) at −10.0 °C.

At 10.00 °C (283.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\ J/K + \frac{-6.00 \times 10^3\ J}{283.15\ K} \\ &= +0.9\ J/K\end{aligned}$$

$\Delta S_{univ} > 0$, so melting *is* spontaneous at 10.00 °C.

Exercise 13.5.1

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of ΔS_{univ}?

Answer

Entropy is a state function, and freezing is the opposite of melting. At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

Summary

The second law of thermodynamics states that a *spontaneous* process increases the entropy of the universe, $S_{univ} > 0$. If $\Delta S_{univ} < 0$, the process is *nonspontaneous*, and if $\Delta S_{univ} = 0$, the system is at equilibrium.

Key Equations

- $\Delta S^\circ = \Delta S^\circ_{298} = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants})$
- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$

Contributors and Attributions

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13.6: The Third Law of Thermodynamics

Learning Objectives

- The *absolute entropy* of a pure substance at a given temperature is the sum of all the entropy it would acquire on warming from absolute zero (where $S = 0$) to the particular temperature.
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure $13.6.1$). The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion (ignoring quantum *zero point motion*).

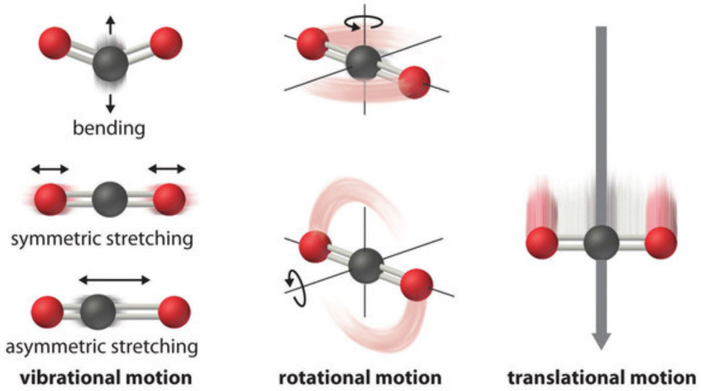

Figure 13.6.1: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion (classically; there will always be motion quantum mechanically) and have zero entropy. In practice, this is an unattainable ideal. (CC BY-SA-NC; Anonymous by request)

This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion (at least classically, quantum mechanics argues for constant motion) means there is but one possible location for each identical atom or molecule comprising the crystal ($\Omega = 1$). According to the Boltzmann equation, the entropy of this system is zero.

$$\begin{aligned} S &= k \ln \Omega \\ &= k \ln(1) \\ &= 0 \end{aligned}$$

In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for the third law of thermodynamics: the entropy of any perfectly ordered, crystalline substance at absolute zero is zero.

Definition: Third Law of Thermodynamics

The entropy of a pure, perfect crystalline substance at 0 K is zero.

The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature. In this section, we examine two different ways to calculate ΔS for a reaction or a physical change. The first, based on the definition of absolute entropy provided by the third law of thermodynamics, uses tabulated values of absolute entropies of substances. The second, based on the fact that entropy is a state function, uses a thermodynamic cycle similar to those discussed previously.

Standard-State Entropies

One way of calculating ΔS for a reaction is to use tabulated values of the standard molar entropy (S^o), which is the entropy of 1 mol of a substance under standard pressure (1 bar). Often the standard molar entropy is given at 298 K and is often demarked as ΔS^o_{298}. The units of S^o are J/(mol•K). Unlike enthalpy or internal energy, it is possible to obtain absolute entropy values by measuring the entropy change that occurs between the reference point of 0 K (corresponding to $S=0$) and 298 K (Tables T1 and T2).

As shown in Table $13.6.1$, for substances with approximately the same molar mass and number of atoms, S^o values fall in the order

$$S^o(\text{gas}) \gg S^o(\text{liquid}) > S^o(\text{solid}). \tag{13.6.1}$$

For instance, S^o for liquid water is 70.0 J/(mol•K), whereas S^o for water vapor is 188.8 J/(mol•K). Likewise, S^o is 260.7 J/(mol•K) for gaseous I_2 and 116.1 J/(mol•K) for solid I_2. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases (Figure $13.6.1$). The correlation between physical state and absolute entropy is illustrated in Figure $13.6.2$, which is a generalized plot of the entropy of a substance versus temperature.

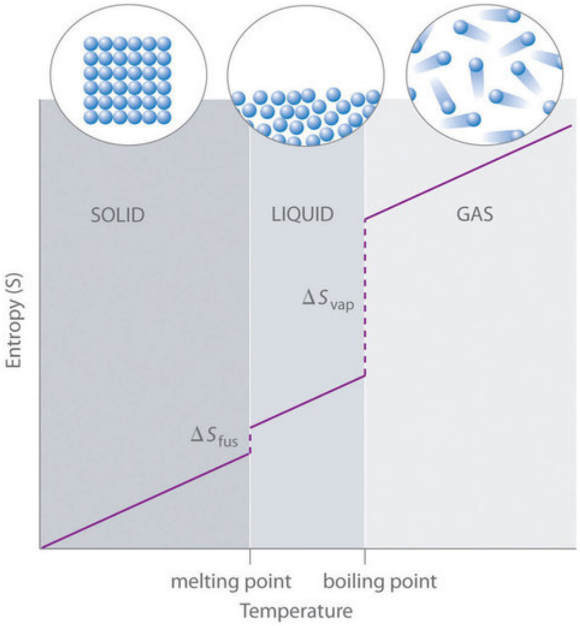

Figure 13.6.2: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (ΔS_{fus}). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas (ΔS_{vap}). (CC BY-SA-NC; anonymous).

The Third Law Lets us Calculate Absolute Entropies

The *absolute entropy* of a substance at any temperature above 0 K must be determined by calculating the increments of heat q required to bring the substance from 0 K to the temperature of interest, and then summing the ratios q/T. Two kinds of experimental measurements are needed:

1. The enthalpies associated with any **phase changes** the substance may undergo within the temperature range of interest. Melting of a solid and vaporization of a liquid correspond to sizeable increases in the number of microstates available to accept thermal energy, so as these processes occur, energy will flow into a system, filling these new microstates to the extent required to maintain a constant temperature (the freezing or boiling point); these inflows of thermal energy correspond to the heats of fusion and vaporization. The entropy increase associated with transition at temperature T is

$$\frac{\Delta H_{fusion}}{T}. \tag{13.6.2}$$

2. The **heat capacity** C of a phase expresses the quantity of heat required to change the temperature by a small amount ΔT, or more precisely, by an infinitesimal amount dT. Thus the entropy increase brought about by warming a substance over a range of temperatures that does not encompass a phase transition is given by the sum of the quantities $C\frac{dT}{T}$ for each increment of temperature dT. This is of course just the integral

$$S_{0\rightarrow T}=\int_0^T \frac{C_p}{T}dt \tag{13.6.3}$$

Because the heat capacity is itself slightly temperature dependent, the most precise determinations of absolute entropies require that the functional dependence of C on T be used in the integral in Equation 13.6.3, i.e.,:

$$S_{0\rightarrow T}=\int_0^T \frac{C_p(T)}{T}dt. \tag{13.6.4}$$

When this is not known, one can take a series of heat capacity measurements over narrow temperature increments ΔT and measure the area under each section of the curve. The area under each section of the plot represents the entropy change associated with heating the substance through an interval ΔT. To this must be added the enthalpies of melting, vaporization, and of any solid-solid phase changes.

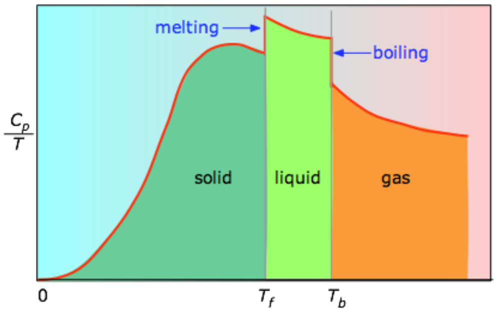

Figure 13.6.3: Heat capacity/temperature as a function of temperature. (CC BY; Stephan Lower)

Values of C_p for temperatures near zero are not measured directly, but can be estimated from quantum theory. The cumulative areas from 0 K to any given temperature (Figure 13.6.3) are then plotted as a function of T, and any phase-change entropies such as

$$S_{vap}=\frac{H_{vap}}{T_b} \tag{13.6.5}$$

are added to obtain the absolute entropy at temperature T. As shown in Figure 13.6.2 above, the entropy of a substance increases with temperature, and it does so for two reasons:

- As the temperature rises, more microstates become accessible, allowing thermal energy to be more widely dispersed. This is reflected in the gradual increase of entropy with temperature.
- The molecules of solids, liquids, and gases have increasingly greater freedom to move around, facilitating the spreading and sharing of thermal energy. Phase changes are therefore accompanied by massive and discontinuous increase in the entropy.

Calculating ΔS_{sys}

We can make careful calorimetric measurements to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. Standard entropies are given the label S^o_{298} for values determined for one mole of substance at a pressure of 1 bar and a temperature of 298 K. The standard entropy change (ΔS^o) for any process may be computed from the standard entropies of its reactant and product species like the following:

$$\Delta S^o=\sum \nu S^o_{298}(\text{products})-\sum \nu S^o_{298}(\text{reactants}) \tag{13.6.6}$$

Here, ν represents stoichiometric coefficients in the balanced equation representing the process. For example, ΔS^o for the following reaction at room temperature

$$m\text{A}+n\text{B}\longrightarrow x\text{C}+y\text{D} \tag{13.6.7}$$

is computed as the following:

$$\Delta S^o = [xS^o_{298}(\mathrm{C}) + yS^o_{298}(\mathrm{D})] - [mS^o_{298}(\mathrm{A}) + nS^o_{298}(\mathrm{B})] \tag{13.6.8}$$

Table 13.6.1 lists some standard entropies at 298.15 K. You can find additional standard entropies in Tables T1 and T2

Table 13.6.1: Standard Molar Entropy Values of Selected Substances at 25°C

Gases		Liquids		Solids	
Substance	*S^o [J/(mol•K)]*	*Substance*	*S^o [J/(mol•K)]*	*Substance*	*S^o [J/(mol•K)]*
He	126.2	H_2O	70.0	C (diamond)	2.4
H_2	130.7	CH_3OH	126.8	C (graphite)	5.7
Ne	146.3	Br_2	152.2	LiF	35.7
Ar	154.8	CH_3CH_2OH	160.7	SiO_2 (quartz)	41.5
Kr	164.1	C_6H_6	173.4	Ca	41.6
Xe	169.7	CH_3COCl	200.8	Na	51.3
H_2O	188.8	C_6H_{12} (cyclohexane)	204.4	MgF_2	57.2
N_2	191.6	C_8H_{18} (isooctane)	329.3	K	64.7
O_2	205.2			NaCl	72.1
CO_2	213.8			KCl	82.6
I_2	260.7			I_2	116.1

A closer examination of Table 13.6.1 also reveals that substances with similar molecular structures tend to have similar S^o values. Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond ($S^o = 2.4\, J/(mol \bullet K)$). In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher S^o (5.7 J/(mol•K)) due to more ~~disorder~~ (microstates) in the crystal. Soft crystalline substances and those with larger atoms tend to have higher entropies because of increased molecular motion and disorder. Similarly, the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the S^o values for CH_3OH(l) and CH_3CH_2OH(l). Finally, substances with strong hydrogen bonds have lower values of S^o, which reflects a more ordered structure.

> *Entropy increases with softer, less rigid solids, solids that contain larger atoms, and solids with complex molecular structures.*

To calculate ΔS^o for a chemical reaction from standard molar entropies, we use the familiar "products minus reactants" rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example 13.6.1 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

✓ Example 13.6.1

Use the data in Table 13.6.1 to calculate ΔS^o for the reaction of liquid isooctane with $O_2(g)$ to give $CO_2(g)$ and $H_2O(g)$ at 298 K.

Given: standard molar entropies, reactants, and products

Asked for: ΔS°

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table 13.6.1. Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain ΔS^o for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

$$C_8H_{18}(l) + \tfrac{25}{2} O_2(g) \longrightarrow 8\,CO_2(g) + 9\,H_2O(g)$$

We calculate ΔS^o for the reaction using the “products minus reactants” rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$\begin{aligned}\Delta S^o_{\text{rxn}} &= \sum mS^o(\text{products}) - \sum nS^o(\text{reactants})\\ &= [8S^o(\text{CO}_2) + 9S^o(\text{H}_2\text{O})] - [S^o(\text{C}_8\text{H}_{18}) + \frac{25}{2}S^o(\text{O}_2)]\\ &= \{[8\text{ mol CO}_2 \times 213.8\text{ J}/(\text{mol}\cdot\text{K})] + [9\text{ mol H}_2\text{O} \times 188.8\text{ J}/(\text{mol}\cdot\text{K})]\}\\ &\quad - \left\{[1\text{ mol C}_8\text{H}_{18} \times 329.3\text{ J}/(\text{mol}\cdot\text{K})] + \left[\frac{25}{2}\text{ mol O}_2 \times 205.2\text{ J}/(\text{mol}\cdot\text{K})\right]\right\}\\ &= 515.3\text{ J}/\text{K}\end{aligned}$$

ΔS^o is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

Exercise 13.6.1

Use the data in Table 13.6.1 to calculate ΔS^o for the reaction of $H_2(g)$ with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}) at 298 K.

Answer

-361.1 J/K

Example 13.6.2: Determination of ΔS°

Calculate the standard entropy change for the following process at 298 K:

$$H_2O(g) \longrightarrow H_2O(l)$$

Solution

The value of the standard entropy change at room temperature, ΔS^o_{298}, is the difference between the standard entropy of the product, $H_2O(l)$, and the standard entropy of the reactant, $H_2O(g)$.

$$\begin{aligned}\Delta S^o_{298} &= S^o_{298}(\text{H}_2\text{O(l)}) - S^o_{298}(\text{H}_2\text{O(g)})\\ &= (70.0\ J\ mol^{-1} K^{-1}) - (188.8\ Jmol^{-1} K^{-1})\\ &= -118.8\ J\ mol^{-1} K^{-1}\end{aligned}$$

The value for ΔS^o_{298} is negative, as expected for this phase transition (condensation), which the previous section discussed.

Exercise 13.6.2

Calculate the standard entropy change for the following process at 298 K:

$$H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)$$

Answer

$-120.6\text{ J mol}^{-1}\text{ K}^{-1}$

Example 13.6.3: Determination of ΔS°

Calculate the standard entropy change for the combustion of methanol, CH_3OH at 298 K:

$$2\,CH_3OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 4\,H_2O(l)$$

Solution

The value of the standard entropy change is equal to the difference between the standard entropies of the products and the entropies of the reactants scaled by their stoichiometric coefficients. The standard entropy of formations are found in Table 13.6.1.

$$\begin{aligned} \Delta S^o &= \Delta S^o_{298} \\ &= \sum \nu S^o_{298}(\text{products}) - \sum \nu S^o_{298}(\text{reactants}) \\ &= 2S^o_{298}(CO_2(g)) + 4S^o_{298}(H_2O(l))] - [2S^o_{298}(CH_3OH(l)) + 3S^o_{298}(O_2(g))] \\ &= [(2 \times 213.8) + (4 \times 70.0)] - [(2 \times 126.8) + (3 \times 205.03)] \\ &= -161.6\ J/mol \cdot K \end{aligned}$$

Exercise 13.6.3

Calculate the standard entropy change for the following reaction at 298 K:

$$Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(l)$$

Answer

24.7 J/mol•K

Summary

Energy values, as you know, are all relative, and must be defined on a scale that is completely arbitrary; there is no such thing as the absolute energy of a substance, so we can arbitrarily define the enthalpy or internal energy of an element in its most stable form at 298 K and 1 atm pressure as zero. The same is *not* true of the entropy; since entropy is a measure of the “dilution” of thermal energy, it follows that the less thermal energy available to spread through a system (that is, the lower the temperature), the smaller will be its entropy. In other words, as the absolute temperature of a substance approaches zero, so does its entropy. This principle is the basis of the *Third law of thermodynamics*, which states that the entropy of a perfectly-ordered solid at 0 K is zero.

In practice, chemists determine the absolute entropy of a substance by measuring the molar heat capacity (C_p) as a function of temperature and then plotting the quantity C_p/T versus T. The area under the curve between 0 K and any temperature T is the absolute entropy of the substance at T. In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only relative terms, not absolute terms.

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe, $S_{\text{univ}} > 0$. If $\Delta S_{\text{univ}} < 0$, the process is nonspontaneous, and if $\Delta S_{\text{univ}} = 0$, the system is at equilibrium. The third law of thermodynamics establishes the zero for entropy as that of a perfect, pure crystalline solid at 0 K. With only one possible microstate, the entropy is zero. We may compute the standard entropy change for a process by using standard entropy values for the reactants and products involved in the process.

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- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

13.7: The Gibbs Free Energy

Learning Objectives

- To understand the relationship between Gibbs free energy and work.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for **both a system and its surroundings**. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient and is provided by a new state function: the Gibbs free energy.

Gibbs Energy and Spontaneity

The Gibbs energy (also known as the *Gibbs function*) is defined as

$$G_{sys} = H_{sys} - TS_{sys} \tag{13.7.1}$$

in which S refers to the entropy of the *system*. Since H, T and S are all state functions, so is G. Thus for any change in state, we can expand Equation 13.7.1 to

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} \tag{13.7.2}$$

How does this simple equation relate to the entropy change of the universe ΔS_{univ} that we know is the sole criterion for spontaneous change from the second law of thermodynamics? Starting with the definition

$$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys} \tag{13.7.3}$$

we would first like to get rid of ΔS_{surr}. How can a chemical reaction (a change in the *system*) affect the entropy of the *surroundings*? Because most reactions are either exothermic or endothermic, they are accompanied by heat q_p across the system boundary (we are considering constant pressure processes). The enthalpy change of the reaction ΔH_{sys} is the "flow" of heat into the system from the surroundings under constant pressure, so the heat "withdrawn" from the surroundings will be $-q_p$.

From the thermodynamic definition of entropy, the change of the entropy of the surroundings will be

$$\Delta S_{surr} = -\frac{q_p}{T} = -\frac{\Delta H_{sys}}{T}. \tag{13.7.4}$$

We can therefore rewrite Equation 13.7.3 as

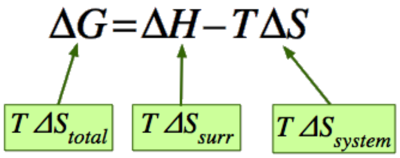
$$\Delta S_{univ} = \frac{-\Delta H_{sys}}{T} + \Delta S_{sys} \tag{13.7.5}$$

Multiplying through by $-T$, we obtain

$$-T\ \Delta S_{univ} = \Delta H_{sys} - T\ \Delta S_{sys} \tag{13.7.6}$$

which expresses the entropy change of the universe in terms of thermodynamic properties of the *system* exclusively.

If $-T\Delta S_{univ}$ is denoted by ΔG, then we have Equation 13.7.2 which defines the *Gibbs energy* change for the process.



The criterion for predicting spontaneity is based on (ΔG), the change in G, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as G. At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S \tag{13.7.7}$$

where all thermodynamic quantities are those of the system. Recall that at constant pressure, $\Delta H = q$, whether a process is reversible or irreversible, and

$$T\Delta S = q_{rev}. \tag{13.7.8}$$

Using these expressions, we can reduce Equation 13.7.7 to

$$\Delta G = q - q_{rev}. \tag{13.7.9}$$

Thus ΔG is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, $q = q_{rev}$ and $\Delta G = 0$. As we shall soon see, if ΔG is zero, the system is at equilibrium, and there will be no net change.

What about processes for which $\Delta G \neq 0$? To understand how the sign of ΔG for a system determines the direction in which change is spontaneous, we can rewrite the relationship between ΔS and q_{rev}, discussed earlier.

$$\Delta S = \frac{q_{rev}}{T}$$

with the definition of ΔH in terms of q_{rev}

$$q_{rev} = \Delta H$$

to obtain

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} \tag{13.7.10}$$

Thus the entropy change of the surroundings is related to the enthalpy change of the system. We have stated that for a spontaneous reaction, $\Delta S_{univ} > 0$, so substituting we obtain

$$\begin{aligned} \Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \\ &= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \end{aligned}$$

Multiplying both sides of the inequality by $-T$ reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0 \tag{13.7.11}$$

which is equal to ΔG (Equation 13.7.7). We can therefore see that for a spontaneous process, $\Delta G_{sys} < 0$.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 13.7.7 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H \ll 0$) that increase the entropy of a system ($\Delta S_{sys} \gg 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995. For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G < 0$, the process occurs spontaneously.
- If $\Delta G = 0$, the system is at equilibrium.
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor.

✓ Example 13.7.1: Vaporizing Water

At Room Temperature (100 °C)

If the conversion of liquid water to water vapor is carried out at 1 atm and the normal boiling point of 100.00 °C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol of water, $\Delta H = 40,657; J$, so the process is highly endothermic. From the definition of ΔS (Equation 13.7.10), we know that for 1 mol of water,

$$\begin{aligned}\Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} \\ &= \frac{\text{40,657 J}}{\text{373.15 K}} \\ &= 108.96\ \text{J/K}\end{aligned}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\begin{aligned}\Delta G_{100^\circ\text{C}} &= \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} \\ &= \text{40,657 J} - [(373.15\ \text{K})(108.96\ \text{J/K})] \\ &= 0\ \text{J}\end{aligned}$$

The energy required for vaporization offsets the increase in entropy of the system. Thus $\Delta G = 0$, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Above Room Temperature (110 °C)

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\begin{aligned}\Delta G_{110^\circ\text{C}} &= \Delta H - T\Delta S \\ &= \text{40,657 J} - [(383.15\ \text{K})(108.96\ \text{J/K})] \\ &= -\text{1,091 J}\end{aligned}$$

Since $\Delta G < 0$, the vaporization of water is predicted to occur spontaneously and irreversibly at 110 °C.

Below Room Temperature (90 °C)

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\begin{aligned}\Delta G_{90^\circ\text{C}} &= \Delta H - T\Delta S \\ &= \text{40,657 J} - [(363.15\ \text{K})(108.96\ \text{J/K})] \\ &= \text{1,088 J}\end{aligned}$$

Since $\Delta G > 0$, water does not spontaneously convert to water vapor at 90 °C. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110°C}$ = 1090 J = −$\Delta G_{90°C}$, as we would predict.

Equilibrium Temperature

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 13.7.7), setting $\Delta G = 0$, and solving for T,

$$\begin{aligned}0 &= 40,657\ J - T(108.96\ J/K) \\ T &= 373.15\ K\end{aligned}$$

Thus $\Delta G = 0$ at $T = 373.15\ K$ and $1\ atm$, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water.

At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 13.7.1 shows how the ΔH and $T\Delta S$ terms vary with temperature for the vaporization of water. When the two lines cross, $\Delta G = 0$, and $\Delta H = T\Delta S$.

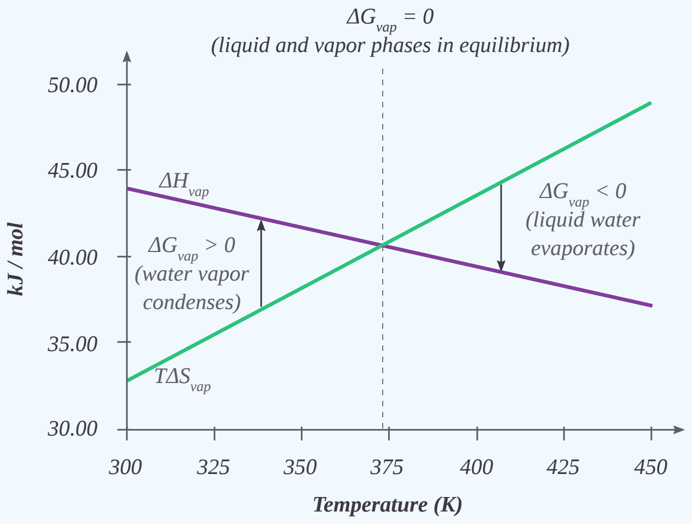


Figure 13.7.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH − TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the $T\Delta S$ term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than $T\Delta S$, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid. (CC BY-NC; Ümit Kaya)

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy ($\Delta H > 0$), which converts the albumin to a highly disordered structure in which the molecules aggregate as a disorganized solid ($\Delta S > 0$). At temperatures greater than 373 K, the $T\Delta S$ term dominates, and $\Delta G < 0$, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.

Figure 13.7.1

ΔH	ΔS	$-T\Delta S$	ΔG
- (exothermic)	+ (products more disordered)	- (favors spontaneity)	- (spontaneous at all T)
- (exothermic)	- (products less disordered)	+ (opposes spontaneity)	- (spontaneous) at low T + (non-spontaneous) at high T **"Enthalpically-driven process"**
+ (endothermic)	+ (products more disordered)	- (favors spontaneity)	+ (non-spontaneous) at low T - (spontaneous) at high T **"Entropically-driven process"**
+ (endothermic)	- (products less disordered)	+ (opposes spontaneity)	+ (non-spontaneous at all T)

Enthalpically vs. Entropically Driving Reactions

Some textbooks and teachers say that the free energy, and thus the spontaneity of a reaction, depends on both the enthalpy and entropy changes of a reaction, and they sometimes even refer to reactions as "energy driven" or "entropy driven" depending on whether ΔH or the $T\Delta S$ term dominates. This is technically correct, but misleading because it disguises the important fact that ΔS_{total}, which this equation expresses in an indirect way, is the *only* criterion of spontaneous change.

Consider the following possible states for two different types of molecules with some attractive force:

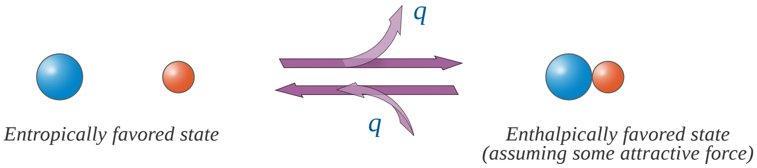


Figure 13.7.2: An enthalpic favored reaction. (CC BY-NC; Ümit Kaya)

There would appear to be greater entropy on the left (state 1) than on the right (state 2). Thus the entropic change for the reaction as written (i.e. going to the right) would be (-) in magnitude, and the energetic contribution to the free energy change would be (+) (i.e. unfavorable) for the reaction as written.

In going to the right, there is an attractive force and the molecules adjacent to each other is a lower energy state (heat energy, q, is liberated). To go to the left, we have to overcome this attractive force (input heat energy) and the left direction is unfavorable with regard to heat energy q. The change in enthalpy is (-) in going to the right (q released), and this enthalpy change is negative (-) in going to the right (and (+) in going to the left). This reaction as written, is therefore, *enthalpically favorable* and *entropically unfavorable*. Hence, It is *enthalpically driven*.

From Table $13.7.1$, it would appear that we might be able to get the reaction to go to the right at low temperatures (lower temperature would minimize the energetic contribution of the entropic change). Looking at the same process from an opposite direction:

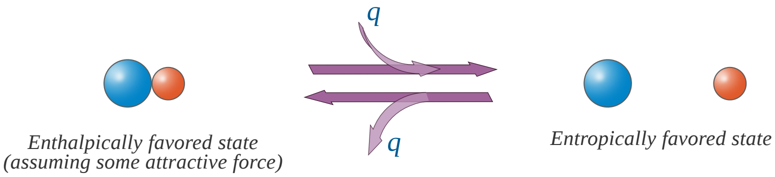


Figure 13.7.3: An entropically favored reaction. (CC BY-NC; Ümit Kaya)

This reaction as written, is *entropically favorable*, and *enthalpically unfavorable;* it is *entropically driven*. From Table $13.7.1$, it would appear that we might be able to get the reaction to go to the right at high temperatures (high temperature would increase the energetic contribution of the entropic change).

The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in Gibbs energy is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure):

$$\Delta G = w_{max}. \tag{13.7.12}$$

To see why this is true, let’s look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 13.7.7. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \tag{13.7.13}$$

This equation tells us that when energy is released during an exothermic process ($\Delta H < 0$), such as during the combustion of a fuel, some of that energy can be used to do work ($\Delta G < 0$), while some is used to increase the entropy of the universe ($T\Delta S > 0$). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table $13.7.2$, the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table $13.7.2$: Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 13.7.14:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{13.7.14}$$

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG^o depends on the relative magnitudes of the ΔH° and TΔS° terms. It is important to recognize that a positive value of ΔG^o for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

> A positive ΔG^o means that the equilibrium constant is less than 1.

Example 13.7.1

Calculate the standard free-energy change (ΔG°) at 25°C for the reaction

$$H_2(g)+O_2(g) \rightleftharpoons H_2O_2(l)$$

At 25°C, the standard enthalpy change (ΔH°) is −187.78 kJ/mol, and the absolute entropies of the products and reactants are:

- S°(H_2O_2) = 109.6 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Is the reaction spontaneous as written?

Given: balanced chemical equation, ΔH° and S° for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A. Calculate ΔS° from the absolute molar entropy values given.
B. Use Equation 13.7.14, the calculated value of ΔS°, and other data given to calculate ΔG^o for the reaction.
C. Use the value of ΔG^o to determine whether the reaction is spontaneous as written.

Solution

A To calculate ΔG^o for the reaction, we need to know ΔH°, ΔS°, and T. We are given ΔH°, and we know that T = 298.15 K. We can calculate ΔS° from the absolute molar entropy values provided using the “products minus reactants” rule:

$$\begin{aligned}\Delta S^\circ &= S^\circ(\mathrm{H_2O_2}) - [S^\circ(\mathrm{O_2}) + S^\circ(\mathrm{H_2})] \\ &= [1 \text{ mol } \mathrm{H_2O_2} \times 109.6 \text{ J}/(\text{mol}\cdot\text{K})] \\ &\quad -\{[1 \text{ mol } \mathrm{H_2} \times 130.7 \text{ J}/(\text{mol}\cdot\text{K})] + [1 \text{ mol } \mathrm{O_2} \times 205.2 \text{ J}/(\text{mol}\cdot\text{K})]\} \\ &= -226.3 \text{ J/K (per mole of } \mathrm{H_2O_2})\end{aligned}$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, ΔS° is very negative for this reaction.

B Substituting the appropriate quantities into Equation 13.7.14,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -187.78 \text{ kJ/mol} - (298.15 \text{ K})[-226.3 \text{ J}/(\text{mol}\cdot\text{K}) \times 1 \text{ kJ}/1000 \text{ J}] \\ &= -187.78 \text{ kJ/mol} + 67.47 \text{ kJ/mol} \\ &= -120.31 \text{ kJ/mol}\end{aligned}$$

The negative value of ΔG^o indicates that the reaction is spontaneous as written. Because ΔS° and ΔH° for this reaction have the same sign, the sign of ΔG^o depends on the relative magnitudes of the ΔH° and TΔS° terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable ΔS° term and for the energy needed to break bonds in the reactants.

Exercise 13.7.1

Calculate the standard free-energy change (ΔG°) at 25°C for the reaction

$$2\,H_2(g)+N_2(g) \rightleftharpoons N_2H_4(l).$$

At 25°C, the standard enthalpy change (ΔH°) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are S°(N_2H_4) = 121.2 J/(mol•K), S°(N_2) = 191.6 J/(mol•K), and S°(H_2) = 130.7 J/(mol•K). Is the reaction spontaneous as written?

Answer

149.5 kJ/mol; no

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG^o for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation (ΔG°_f)of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $\Delta G^\circ_f = 0$. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation (ΔH°_f) and the standard entropy of formation (ΔS°_f) using the definition of free energy:

$$\Delta G^o_f = \Delta H^o_f - T\Delta S^o_f \tag{13.7.15}$$

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar "products minus reactants" rule:

$$\Delta G^o_{rxn} = \sum m\Delta G^o_f(products) - \sum n\Delta G^o_f(reactants) \tag{13.7.16}$$

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG^o indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

"Products minus Reactants" Rule

The ΔG^o of a reaction can be calculated from tabulated ΔG^o_f values (Table T1) using the "products minus reactants" rule.

Example 13.7.2

Calculate ΔG^o for the reaction of isooctane with oxygen gas to give carbon dioxide and water. Use the following data:

- ΔG°_f(isooctane) = −353.2 kJ/mol,
- $\Delta G^\circ_f(CO_2)$ = −394.4 kJ/mol, and
- $\Delta G^\circ_f(H_2O)$ = −237.1 kJ/mol.

Is the reaction spontaneous as written?

Given: balanced chemical equation and values of ΔG°_f for isooctane, CO_2, and H_2O

Asked for: spontaneity of reaction as written

Strategy:

Use the "products minus reactants" rule to obtain ΔG°_{rxn}, remembering that ΔG°_f for an element in its standard state is zero. From the calculated value, determine whether the reaction is spontaneous as written.

Solution

The balanced chemical equation for the reaction is as follows:

$$\mathrm{C_8H_{18}(l) + \tfrac{25}{2}O_2(g) \longrightarrow 8\,CO_2(g) + 9\,H_2O(l)}$$

We are given ΔG°_f values for all the products and reactants except $O_2(g)$. Because oxygen gas is an element in its standard state, ΔG°_f (O_2) is zero. Using the "products minus reactants" rule,

$$\begin{aligned}
\Delta G^\circ &= [8\Delta G^\circ_\mathrm{f}(\mathrm{CO_2}) + 9\Delta G^\circ_\mathrm{f}(\mathrm{H_2O})] - \left[1\Delta G^\circ_\mathrm{f}(\mathrm{C_8H_{18}}) + \frac{25}{2}\Delta G^\circ_\mathrm{f}(\mathrm{O_2})\right] \\
&= [(8\text{ mol})(-394.4\text{ kJ/mol}) + (9\text{ mol})(-237.1\text{ kJ/mol})] \\
&- \left[(1\text{ mol})(-353.2\text{ kJ/mol}) + \left(\frac{25}{2}\text{ mol}\right)(0\text{ kJ/mol})\right] \\
&= -4935.9\text{ kJ (per mol of }\mathrm{C_8H_{18}})
\end{aligned}$$

Because ΔG^o is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG^o is largely determined by the ΔG°_f of the stable products: water and carbon dioxide.

Exercise 13.7.2

Calculate ΔG^o for the reaction of benzene with hydrogen gas to give cyclohexane using the following data

- ΔG°_f(benzene) = 124.5 kJ/mol
- ΔG°_f (cyclohexane) = 217.3 kJ/mol.

Is the reaction spontaneous as written?

Answer

92.8 kJ; no

Calculated values of ΔG^o are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of ΔG^o may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from ΔG°. If the ΔH and TΔS terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG^o at various temperatures, as long as no phase change occurs over the temperature range being considered.

> In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Example 13.7.3

Calculate (a) ΔG^o and (b) $\Delta G_{300°C}$ for the reaction $N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)$, assuming that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

- $S°(N_2)$ = 191.6 J/(mol•K),
- $S°(H_2)$ = 130.7 J/(mol•K),
- $S°(NH_3)$ = 192.8 J/(mol•K), and
- ΔH°_f (NH_3) = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, S° values, and ΔH°_f for NH_3

Asked for: ΔG^o and ΔG at 300°C

Strategy:

A. Convert each temperature to kelvins. Then calculate ΔS° for the reaction. Calculate ΔH° for the reaction, recalling that ΔH°_f for any element in its standard state is zero.
B. Substitute the appropriate values into Equation 13.7.14to obtain ΔG^o for the reaction.
C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation 13.7.7to obtain ΔG for the reaction at 300°C.

Solution

A To calculate ΔG^o for the reaction using Equation 13.7.14, we must know the temperature as well as the values of ΔS° and ΔH°. At standard conditions, the temperature is 25°C, or 298 K. We can calculate ΔS° for the reaction from the absolute molar entropy values given for the reactants and the products using the “products minus reactants” rule:

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= 2S^\circ(\text{NH}_3) - [S^\circ(\text{N}_2) + 3S^\circ(\text{H}_2)] \\ &= [2 \text{ mol NH}_3 \times 192.8 \text{ J}/(\text{mol}\cdot\text{K})] \\ &\quad - \{[1 \text{ mol N}_2 \times 191.6 \text{ J}/(\text{mol}\cdot\text{K})] + [3 \text{ mol H}_2 \times 130.7 \text{ J}/(\text{mol}\cdot\text{K})]\} \\ &= -198.1 \text{ J/K (per mole of N}_2)\end{aligned}$$

We can also calculate ΔH° for the reaction using the “products minus reactants” rule. The value of ΔH°_f (NH_3) is given, and ΔH°_f is zero for both N_2 and H_2:

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= 2\Delta H^\circ_f(\text{NH}_3) - [\Delta H^\circ_f(\text{N}_2) + 3\Delta H^\circ_f(\text{H}_2)] \\ &= [2 \times (-45.9 \text{ kJ/mol})] - [(1 \times 0 \text{ kJ/mol}) + (3 \times 0 \text{ kJ/mol})] \\ &= -91.8 \text{ kJ(per mole of N}_2)\end{aligned}$$

B Inserting the appropriate values into Equation 13.7.14

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= \Delta H^\circ - T\Delta S^\circ \\ &= (-91.8 \text{ kJ}) - (298 \text{ K})(-198.1 \text{ J/K})(1 \text{ kJ}/1000 \text{ J}) \\ &= -32.7 \text{ kJ (per mole of N}_2)\end{aligned}$$

C To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300°C}$ = H° and $\Delta S_{300°C}$ = ΔS°) and insert the appropriate temperature (573 K) into Equation 13.7.7:

$$\begin{aligned}\Delta G_{300^\circ\text{C}} &= \Delta H_{300^\circ\text{C}} - (573 \text{ K})(\Delta S_{300^\circ\text{C}}) \\ &= \Delta H^\circ - (573 \text{ K})\Delta S^\circ \\ &= (-91.8 \text{ kJ}) - (573 \text{ K})(-198.1 \text{ J/K})(1 \text{ kJ}/1000 \text{ J}) \\ &= 21.7 \text{ kJ (per mole of N}_2)\end{aligned}$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is thermodynamically spontaneous, but in practice, it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more rapidly also changes the thermodynamics by causing the −TΔS° term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its K_{eq} is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

? Exercise 13.7.3

Calculate

a. ΔG° and
b. $\Delta G_{750^\circ C}$

for the following reaction

$$2\,\text{NO(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\,\text{NO}_2\text{(g)}$$

which is important in the formation of urban smog. Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

- S°(NO) = 210.8 J/(mol•K),
- $S^\circ(O_2)$ = 205.2 J/(mol•K),
- $S^\circ(NO_2)$ = 240.1 J/(mol•K),
- $\Delta H^\circ_f(NO_2)$ = 33.2 kJ/mol, and
- ΔH°_f (NO) = 91.3 kJ/mol.

Answer a

−72.5 kJ/mol of O_2

Answer b

33.8 kJ/mol of O_2

The effect of temperature on the spontaneity of a reaction, which is an important factor in the design of an experiment or an industrial process, depends on the sign and magnitude of both ΔH° and ΔS°. The temperature at which a given reaction is at equilibrium can be calculated by setting ΔG^o = 0 in Equation 13.7.14, as illustrated in Example 13.7.4.

✓ Example 13.7.4

As you saw in Example 13.7.3, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which ΔH° and ΔS° are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 13.7.3 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

Given: ΔH° and ΔS°

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set ΔG^o equal to zero in Equation 13.7.14 and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution

In Example 13.7.3, we calculated that ΔH° is −91.8 kJ/mol of N_2 and ΔS° is −198.1 J/K per mole of N_2, corresponding to ΔG^o = −32.7 kJ/mol of N_2 at 25°C. Thus the reaction is indeed spontaneous at low temperatures, as expected based on the signs of ΔH° and ΔS°. The temperature at which the reaction becomes nonspontaneous is found by setting ΔG^o equal to zero and rearranging Equation 13.7.14 to solve for T:

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 0 \\ \Delta H^\circ &= T\Delta S^\circ \\ T = \frac{\Delta H^\circ}{\Delta S^\circ} &= \frac{(-91.8\text{ kJ})(1000\text{ J/kJ})}{-198.1\text{ J/K}} = 463\text{ K} \end{aligned}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

? Exercise 13.7.4

As you found in the exercise in Example 13.7.3, ΔH° and ΔS° are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

Answer

792.6 K

Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.
- Free-energy change

$$\Delta G = \Delta H - T\Delta S$$

- Standard free-energy change

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called Gibbs free energy (G). The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, ΔG = 0. If the process is spontaneous, ΔG < 0. If the process is not spontaneous as written but is spontaneous in the reverse direction, ΔG > 0. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free energy of formation (ΔG°_f), is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate ΔG^o for a reaction.

Contributors and Attributions

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13.8: Carnot Cycle, Efficiency, and Entropy

In the early 19th century, steam engines came to play an increasingly important role in industry and transportation. However, a systematic set of theories of the conversion of thermal energy to motive power by steam engines had not yet been developed. Nicolas Léonard Sadi Carnot (1796-1832), a French military engineer, published *Reflections on the Motive Power of Fire* in 1824. The book proposed a generalized theory of heat engines, as well as an idealized model of a thermodynamic system for a heat engine that is now known as the Carnot cycle. Carnot developed the foundation of the second law of thermodynamics, and is often described as the "Father of thermodynamics."

The Carnot Cycle

The Carnot cycle consists of the following four processes:

I. A reversible isothermal gas expansion process. In this process, the ideal gas in the system absorbs q_{in} amount heat from a heat source at a high temperature T_{high} , expands and does work on surroundings.
II. A reversible adiabatic gas expansion process. In this process, the system is thermally insulated. The gas continues to expand and do work on surroundings, which causes the system to cool to a lower temperature, T_{low}.
III. A reversible isothermal gas compression process. In this process, surroundings do work to the gas at T_{low}, and causes a loss of heat, q_{out}.
IV. A reversible adiabatic gas compression process. In this process, the system is thermally insulated. Surroundings continue to do work to the gas, which causes the temperature to rise back to T_{high} .

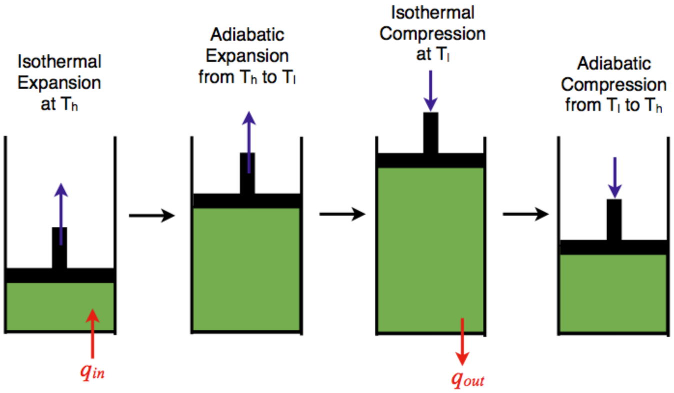

Figure 13.8.1: An ideal gas-piston model of the Carnot cycle. (CC BY 4.0; XiSen Hou via Hope College)

P-V Diagram

The P-V diagram of the Carnot cycle is shown in Figure 13.8.2 In isothermal processes I and III, ΔU=0 because ΔT=0. In adiabatic processes II and IV, q=0. Work, heat, ΔU, and ΔH of each process in the Carnot cycle are summarized in Table 13.8.1.

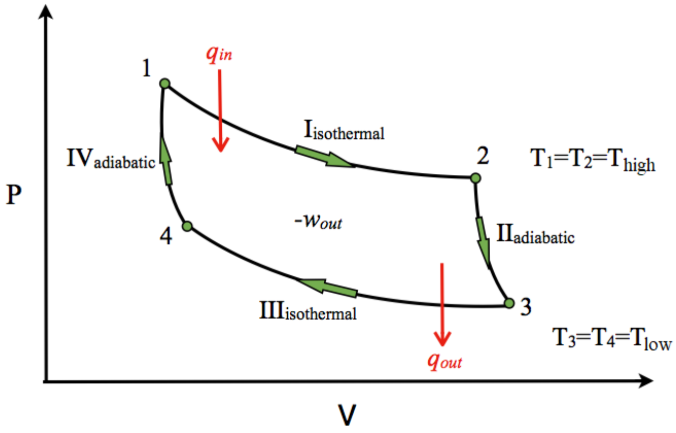

Figure 13.8.2: A P-V diagram of the Carnot Cycle.

Table 13.8.1: Work, heat, ΔU, and ΔH in the P-V diagram of the Carnot Cycle.

Process	*w*	*q*	ΔU	ΔH
I	$-nRT_{high}\ln\left(\frac{V_2}{V_1}\right)$	$nRT_{high}\ln\left(\frac{V_2}{V_1}\right)$	0	0
II	$n\bar{C}_v(T_{low}-T_{high})$	0	$n\bar{C}_v(T_{low}-T_{high})$	$n\bar{C}_p(T_{low}-T_{high})$
III	$-nRT_{low}\ln\left(\frac{V_4}{V_3}\right)$	$nRT_{low}\ln\left(\frac{V_4}{V_3}\right)$	0	0
IV	$n\bar{C}_v(T_{high}-T_{low})$	0	$n\bar{C}_v(T_{hight}-T_{low})$	$n\bar{C}_p(T_{high}-T_{low})$
Full Cycle	$-nRT_{high}\ln\left(\frac{V_2}{V_1}\right)-nRT_{low}\ln\left(\frac{V_4}{V_3}\right)$	$nRT_{high}\ln\left(\frac{V_2}{V_1}\right)+nRT_{low}\ln\left(\frac{V_4}{V_3}\right)$	0	0

T-S Diagram

The T-S diagram of the Carnot cycle is shown in Figure 13.8.3. In isothermal processes I and III, ΔT=0. In adiabatic processes II and IV, ΔS=0 because dq=0. ΔT and ΔS of each process in the Carnot cycle are shown in Table 13.8.2.

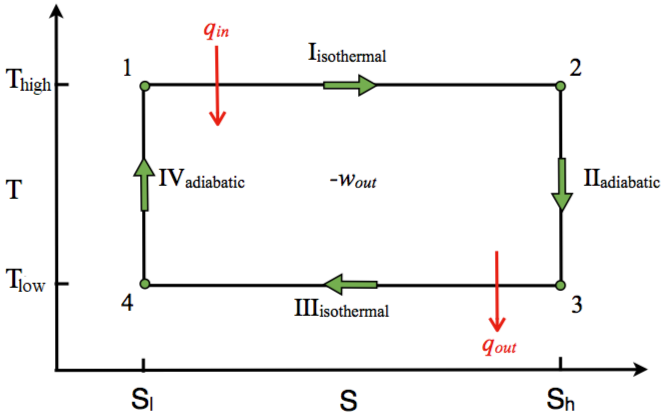

Figure 13.8.3: A T-S diagram of the Carnot Cycle. (CC BY 4.0; XiSen Hou via Hope College)

Table 13.8.1: Work, heat, and ΔU in the T-S diagram of the Carnot Cycle.

Process	**ΔT**	**ΔS**
I	0	$-nR\ln\left(\frac{V_2}{V_1}\right)$
II	$T_{low}-T_{high}$	0
III	0	$-nR\ln\left(\frac{V_4}{V_3}\right)$
IV	$T_{high}-T_{low}$	0
Full Cycle	0	0

Efficiency

The Carnot cycle is the most efficient engine possible based on the assumption of the absence of incidental wasteful processes such as friction, and the assumption of no conduction of heat between different parts of the engine at different temperatures. The efficiency of the carnot engine is defined as the ratio of the energy output to the energy input.

$$\begin{aligned}\text{efficiency} &= \frac{\text{net work done by heat engine}}{\text{heat absorbed by heat engine}} \\ &= \frac{-w_{sys}}{q_{high}} \\ &= \frac{nRT_{high}\ln\left(\dfrac{V_2}{V_1}\right) + nRT_{low}\ln\left(\dfrac{V_4}{V_3}\right)}{nRT_{high}\ln\left(\dfrac{V_2}{V_1}\right)}\end{aligned}$$

Since processes II (2-3) and IV (4-1) are adiabatic,

$$\left(\frac{T_2}{T_3}\right)^{C_V/R} = \frac{V_3}{V_2}$$

and

$$\left(\frac{T_1}{T_4}\right)^{C_V/R} = \frac{V_4}{V_1}$$

And since $T_1 = T_2$ and $T_3 = T_4$,

$$\frac{V_3}{V_4} = \frac{V_2}{V_1}$$

Therefore,

$$\text{efficiency} = \frac{nRT_{high}\ln\left(\dfrac{V_2}{V_1}\right) - nRT_{low}\ln\left(\dfrac{V_2}{V_1}\right)}{nRT_{high}\ln\left(\dfrac{V_2}{V_1}\right)}$$

$$\boxed{\text{efficiency} = \frac{T_{high} - T_{low}}{T_{high}}}$$

Summary

The Carnot cycle has the greatest efficiency possible of an engine (although other cycles have the same efficiency) based on the assumption of the absence of incidental wasteful processes such as friction, and the assumption of no conduction of heat between different parts of the engine at different temperatures.

Problems

1. You are now operating a Carnot engine at 40% efficiency, which exhausts heat into a heat sink at 298 K. If you want to increase the efficiency of the engine to 65%, to what temperature would you have to raise the heat reservoir?
2. A Carnot engine absorbed 1.0 kJ of heat at 300 K, and exhausted 400 J of heat at the end of the cycle. What is the temperature at the end of the cycle?
3. An indoor heater operating on the Carnot cycle is warming the house up at a rate of 30 kJ/s to maintain the indoor temperature at 72 ºF. What is the power operating the heater if the outdoor temperature is 30 ºF?

References

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13.E: Spontaneous Processes (Exercises)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

Q3

Write detailed calculation down for each question involved in gambling,

a. How many “microstates” are there for the cards that come up from five random cards each from a separate deck?
b. What is the probability of getting 5 queens of hearts?
c. What is the probability of getting any specific hand of five cards?

Solution

Microstates are specific configurations in which each particle is distinguishable. The number of ways that they can be arranged to describe the macrostate is the weight of that macrostate and used in the definition of entropy.

a. The number of possible outcomes (microstates) of any repeated independent situation is equal to the number of possibilities in one iteration to the power of the repetitions. So in this case, the answer is 52 to the power of 5.
b. One of these 52^5 possibilities.
c. One of these 52^5 possibilities.

Q5

Is the above reaction spontaneous under 1 atm and room temperature? If so, what are the driving factors?

$$3\,\mathrm{NO(g)} \rightleftharpoons \mathrm{N_2O(g)} + \mathrm{NO_2(g)}$$

Solution

From a superficial overview of the reaction, we would conclude that the enthalpy change would be negative (i.e., $\Delta H < 0$) (why? more bonding in the products than the reactants). We would also expect a negative value of entropy ($\Delta n_{gas} < 0$. It is difficult to argue which would win from just looking at the reaction and we need to do a Hess's law like approach to solve numerically using the Gibbs energies of formation from Table T1:

$$\Delta^o G_{rxn} = \Delta^o G_f\{N_2O\} + \Delta G_f^o\{NO_2\} - 3\Delta G_f^o\{NO\}$$

Q9

For each of the following scenarios predict the system's entropy change whether it is $\Delta S < 0$, $\Delta S = 0$, or $\Delta S > 0$.

a. Increasing the amount of quarters being flipped from 2 to 4.
b. Moving a child from a 30 ft. × 30 ft. room to a 5 ft. × 5 ft. room to play in .
c. Increasing the temperature of a non-ideal polyatomic gas.

Solution

a. Increasing the amount of flipped quarters leads to ($\Delta S > 0$) because it increases the number of microstates available. For example: $2^2 = 4$ so 4 microstates possible with 2 quarters but $2^4 = 16$ so 16 microstates are available with four quarters. 16 > 4 so entropy would increase.
b. If you divided the room in 1 sq. ft cubes as the places where the child may stand/play, there are only 25 squares in which the child could stand so 25 microstates versus 900 squares/microstates in the other room. Therefore $\Delta S < 0$ because there are less microstates available.
c. Increasing the temperature of a non-ideal gas would lead to ($\Delta S > 0$) because the increased temperature would "unfreeze" "frozen" modes in the gas, which would allow it more degrees of freedom and therefore microstates.

Q10

Determine whether the change in entropy for the processes listed down below are positive or negative:

a. condensing of iodine gas into a solid

b. diffusion of an ideal gas

Solution

a. Change in entropy is negative, as gaseous iodine turns solid, the decreased freedom of movement restricts the possible particle locations and hence there is a decrease in the number of microstates.
b. Change of entropy is positive. As diffusion occurs, there is increased freedom of movement and increase in the possible particle locations and an increase in the number of microstates.

Q11

Osmium melts at 3,027 °C and has an enthalpy change of fusion of 31.0 kJ/mol. Calculate the entropy of fusion of osmium.

Solution

Define the system at 1 mole of solid osmium at its melting point of 3027°C (3300 K). Imagine adding 31.0 kJ of heat infinitely slowly in such a way that the temperature remains constant, as the osmium melts. The heat is then equal to the q_{rev} for the melting. Substitute the value of heat supplied and T into the equation that defines the entropy of the change of the entropy of a system. Because the change occurs at a constant temperature, T may be outside the integral sign

$$\Delta S = \int \frac{dq_{rev}}{T} = \frac{1}{T}\int dq_{rev} = \frac{1}{T}q_{rev} = \frac{31.0 \times 10^3\ J\ mol^{-1}}{3300\ K} = 9.39\ J\ K^{-1}\ mol^{-1}$$

Tip. The temperature must be an absolute temperature (in Kelvins, for example).

Q13

Trouton's Rule is used to estimate the molar enthalpy of vaporization. What is iodine's enthalpy of vaporization if its normal boiling point is 184.4^{o}C?

Solution

Trouton's Rule:

$$\Delta H_{vap} = \Delta S_{vap} T_b \tag{13.E.1}$$

$$\Delta S_{vap} \approx 88 \frac{J}{Kmol} \tag{13.E.2}$$

$$T_b = 184.4^o C = 457.55 K \tag{13.E.3}$$

$$\Delta H_{vap} = (88 \frac{J}{Kmol})(457.55K) = 40264.4 \frac{J}{mol} = 40.26 \frac{kJ}{mol} \tag{13.E.4}$$

Enthalpy of vaporization of iodine is 40.26 kJ/mol

Q15

If 0.250 mol Argon is expanded reversibly and isothermally at 400 K in its compressible oven from an initial volume of 12.0 L to a final volume of 30.0 L, what will the ΔU, q, w, ΔH, and ΔS for the gas?

Solution

For an isothermal process, ΔU = 0, and consequently, ΔH = 0. However, for the work:

$$w = \int_{v_o}^{v_f} P\, dV$$

Where:

$$P = \frac{nRT}{V}$$

meaning that if we put P into terms of V using PV=nRT, then we can get the work, which comes out look like:

$$w = nRT \ln \frac{V_f}{V_o}$$

$$w = (0.250\ mol) \times (8.314\ \frac{\text{J}}{\text{Kmol}}) \times (400\ \text{K}) \times \ln \frac{30.0\ L}{12.0\ L} = 761.8\ \text{J}$$

$PV = nRT$ is the ideal gas law. it implies that the molecules or atoms of the gas are point masses, they have no volume and undergo only elastic collision.

Therefore, by the first law, the heat, q, must be be the negative of the work. Now, as for ΔS, we know:

$$\Delta S = \frac{-q}{T}$$

which implies that:

$$\Delta S = nR \ln \frac{V_f}{V_o}$$

$$\Delta S = (0.250\ \text{mol}) \times (8.314\ \frac{\text{J}}{\text{Kmol}}) \times \ln \frac{30.0\ \text{L}}{12.0\ \text{L}} = 1.90\ \frac{\text{J}}{\text{K}}$$

Q17

Consider this. Exactly 2 moles of ice undergoes three different processes.

I. heated reversibly at atmospheric pressure from temperature X to 0 °C, then
II. melted reversibly at 0 °C. Finally
III. it was heated reversibly at atmospheric pressure up to an unknown temperature Y.

Find temperature X & Y and identify ΔS_{surr}.

Given:

- ΔH_{fus} = 6007 J.mol^{-1}
- C_p (ice) = 38 J.K^{-1}.mol^{-1}
- C_p (water) = 75 J.K^{-1}.mol^{-1}
- ΔS_{I} = 12.034 J.K^{-1}
- ΔS_{III} = 136 J.K^{-1}

Solution

Since entropy changes are additive (thanks for them being state functions) and we have the entropy changes for Step I and Step III, all we need to do is calculate ΔS_{II}. However, we need to calculate temperatures first.

The equation below can be used to calculate ΔS_{sys} for a temperature change.

$$\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right) \tag{13.E.5}$$

To solve for unknown temperature, the equation can be arranged in this way.

$$\exp(\frac{\Delta S}{nC_p}) = \frac{T_2}{T_1} \tag{13.E.6}$$

Assuming the C_p stays constant throughout all the temperature change. Initial temperature X and final temperature Y can be found using the formula below.

$$T_x = T_2(\exp(\frac{\Delta S_{\text{I}}}{nC_p}))^{-1} = (273.15K)(\exp(\frac{12.034J.K^{-1}}{(2.00mol)(38J.K^{-1}.mol^{-1})}))^{-1} = 233.15K \tag{13.E.7}$$

$$T_y = T_1(\exp(\frac{\Delta S_{\text{III}}}{nC_p})) = (273.15K)(\exp(\frac{136J.K^{-1}}{(2.00mol)(75J.K^{-1}.mol^{-1})})) = 298.15K \tag{13.E.8}$$

ΔS_{II} must also be determined to obtain the ΔS_{system}.

Since the temperature remains constant in the second step, $\Delta S = q_{rev}$.

$$\Delta S_{\text{II}} = 2\, mol \times \frac{6007\ J/mol}{273.15\ K} = 43.984\ J.K^{-1} \tag{13.E.9}$$

Since the entire process is reversible,

$$\Delta \text{S}_{\text{surr}} + \Delta \text{S}_{\text{system}} = 0$$

so

$$\Delta \text{S}_{\text{surr}} = -\Delta \text{S}_{\text{system}}.$$

Now we add the three entropy changes:

$$-\Delta S_{\text{system}} = -(\Delta S_{\text{I}} + \Delta S_{\text{II}} + \Delta S_{\text{III}}) \tag{13.E.10}$$

$$= -(12.034 + 54.98 + 136) J.K^{-1} \tag{13.E.11}$$

$$= -80.15\ J.K^{-1} \tag{13.E.12}$$

$$= \Delta S_{\text{surr}} \tag{13.E.13}$$

Q18

Suppose 2 moles of water at standard temperature (25°C) and pressure is spontaneously evaporated by allowing it to fall onto a nickel plate maintained at 125°C. Calculate ΔS for the water, ΔS for the nickel plate, and ΔS_{total} if $C_{p(\text{H}_2\text{O})(\text{l})}$= 75.4 J/(K.mol) and $C_{p(\text{H}_2\text{O})(\text{g})}$ = 36.0 J/(K.mol). Take ΔH_{vap} = 40.68 KJ/mol for water and its boiling point of 100°C.

Solution

$$q_1 = \Delta H = mc\Delta T = 2 \times 75.4 \frac{J}{K.mol} \times (100 - 25) = 11310\ J \tag{13.E.14}$$

$$q_2 = 40680 \frac{J}{mol} \times 2 = 81.36 \times 10^3\ J \tag{13.E.15}$$

$$q_3 = \Delta H = mc\Delta T = 2 \times 36 \frac{J}{K.mol} \times (125 - 100) = 1800\ J \tag{13.E.16}$$

$$q_{total} = 11310 + 81.36 \times 10^3 + 1800 = 94470\ J \tag{13.E.17}$$

$$\Delta S_{\text{H}_2\text{O}} = nC_{p(\text{H}_2\text{O(l)})}) \ln \frac{T_2}{T_1} + nC_p(H_2O(g)) \ln \frac{T_2}{T_1} + n\frac{\Delta H}{T} \tag{13.E.18}$$

$$= (2 \times 75.4 \times \ln \frac{373}{298}) + (2 \times 36 \times \ln \frac{398}{373}) + (2 \times \frac{40680}{373}) = 256.6 \frac{J}{K} \tag{13.E.19}$$

$$\Delta S_{iron} = \frac{-94470J}{398K} = -237.4 \frac{J}{K} \tag{13.E.20}$$

$$\Delta S_{tot} = \Delta S_{\text{H}_2\text{O}} + \Delta S_{\text{iron}} = 19.2 \frac{J}{K} \tag{13.E.21}$$

Q19

A 181.49 g sample of lead at 97.0$^{\text{o}}$C initially is added to a coffee cup calorimeter that contains 150.0 g water which is at 24.7$^{\text{o}}$C. The equilibrium temperature is 29.4$^{\text{o}}$C, assuming that there is no heat lost to the calorimeter or the environment. The molar heat capacity of lead (C_p(Pb)) is 26.4 J K^{-1} mol^{-1} and that of water (C_p(H_2O)) is 75.2 J K^{-1} mol^{-1}. What is ΔS for the lead sample, ΔS for the water sample, and ΔS_{total} for this process?

Solution

Since this progress is carried out at a constant pressure, and the temperature change for this progress doesn't include a phase transition, the relationship between the ΔS and the ΔT of a system can be described as:

$$\Delta S = nc_p ln\left(\frac{T_2}{T_1}\right) \tag{13.E.22}$$

Convert the temperatures to Kelvin:

$$T_{equilibrium} = (29.4 + 273.15)K = 302.55\ K \tag{13.E.23}$$

$$T_{initial,\ Pb} = (97.0 + 273.15)K = 370.15\ K \tag{13.E.24}$$

$$T_{initial,\ H_2O} = (24.7 + 273.15)K = 297.85\ K \tag{13.E.25}$$

Calculate the amount of moles of the substance present:

$$n_{Pb} = 181.49\ g\ Pb \times \frac{1\ mol\ Pb}{207.2\ g\ Pb} = 0.8759\ mol\ Pb \tag{13.E.26}$$

$$n_{H_2O} = 150.0\ g\ H_2O \times \frac{1\ mol\ H_2O}{18.02\ g\ H_2O} = 8.324\ mol\ H_2O \tag{13.E.27}$$

The given molar heat capacities:

$$C_{p,\ Pb} = 26.4\frac{J}{K \cdot mol} \tag{13.E.28}$$

$$C_{p,\ H_2O} = 75.2\frac{J}{K \cdot mol} \tag{13.E.29}$$

Substitute the known variables into the equation: $\Delta S = nc_p ln\left(\frac{T_2}{T_1}\right)$

$$\Delta S_{Pb} = nc_{p,Pb} ln\left(\frac{T_{equilibrium}}{T_{inital,\ Pb}}\right) \tag{13.E.30}$$

$$\Delta S_{Pb} = 0.8759\ mol\ Pb \times 26.4\frac{J}{K \cdot mol} \times ln\left(\frac{302.55\ K}{370.15\ K}\right) = -4.66\ \frac{J}{K} \tag{13.E.31}$$

$$\Delta S_{H_2O} = nc_{p,H_2O} ln\left(\frac{T_{equilibrium}}{T_{inital,\ H_2O}}\right) \tag{13.E.32}$$

$$\Delta S_{H_2O} = 8.324\ mol\ H_2O \times 75.2\frac{J}{K \cdot mol} \times ln\left(\frac{302.55\ K}{297.85\ K}\right) = 9.80\ \frac{J}{K} \tag{13.E.33}$$

$$\Delta S_{total} = \Delta S_{Pb} + \Delta S_{H_2O} = (-4.66 + 9.80)\ \frac{J}{K} = 5.14\ \frac{J}{K} \tag{13.E.34}$$

Q20

Copper has a heat capacity of 38.5 J K^{-1} mol^{-1}, approximately independent of temperature between 0°C to 100°C. Calculate the enthalpy and entropy change of 5.00 moles of copper as it is cooled at atmospheric pressure from 100°C to 0°C.

Solution

$$\Delta H = q = nC_p\Delta T \tag{13.E.35}$$

$$= (5.00\ mol)(38.5\ \frac{J}{K.mol})(273\ K - 373\ K)$$

$$\Delta H = -19250\ J$$

$$\Delta S = nC_p ln(\frac{T_2}{T_1}) \tag{13.E.36}$$

$$= (38.5\frac{J}{K.mol})\ln(\frac{273\ K}{373\ K})(5.00\ mol)$$

$$= -60.1\frac{J}{K}$$

Q23

The alkaline earth metals react with oxygen to give the following compounds:

$$2\,Be(g) + O_2(g) \longrightarrow 2\,BeO(s)$$

$$2\,Mg(g) + O_2(g) \longrightarrow 2\,MgO(s)$$

$$2\,Ca(g) + O_2(g) \longrightarrow 2\,CaO(s)$$

Compute ΔS for each reaction, and identify a periodic trend about the entropy.

Solution

All the values you need to solve this problem are in the back of the Oxtoby textbook, so just find the numbers needed and use the formula:

$$\sum S^o_{products} - \sum S^o_{reactants} = \Delta S^o_{rxn}$$

$$2Be_{(g)} + O_{2(g)} \rightarrow 2BeO_{(s)}$$

$$2(14.14) - (2(136.16) + 205.03) = -449.07 \frac{\text{J}}{\text{K. mol}}$$

$$2Mg_{(g)} + O_{2(g)} \rightarrow 2MgO_{(s)}$$

$$2(26.92) - (2(148.54) + 205.03) = -448.27 \frac{\text{J}}{\text{K. mol}}$$

$$2Ca_{(g)} + O_{2(g)} \rightarrow 2CaO_{(s)}$$

$$2(39.75) - (2(154.77) + 205.03) = -435.07 \frac{\text{J}}{\text{K. mol}}$$

The entropy of the reaction decreases as you go up the periodic table.

Q27

Is the entropy change in the reaction positive, negative or zero and why?

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$$

Hint: You don't need to actually calculate the change in entropy to determine whether the change in entropy is positive or negative. Think about it conceptually.

Solution

The answer is negative because the number of gas molecules decreases. Gas molecules have more entropy than liquid molecules since they have more energy in the form of degrees of freedom of motion (translational, rotational, and vibrational). Therefore, fewer gas molecules mean less entropy.

Q33

At $25.0^\circ\text{C}$the reaction below is not spontaneous.

$$2\,H_2O(g) \longrightarrow 2\,H_2(g) + O_2(g)$$

with $\Delta G = +228.59\ \frac{kJ}{mol}$

If the above reaction were coupled with the following nonspontaneous reaction, could it be made to proceed? Why or Why not?

$$3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$$

with $\Delta G = -16.48\ \frac{kJ}{mol}$

Solution

Coupling the nonspontaneous reaction

$$2\,H_2O_{(g)} \rightleftharpoons 2\,H_{2\ (g)} + O_{2\ (g)}$$

with $\Delta G = +228.59\ \frac{kJ}{mol}$

for a spontaneous reaction (ΔG) is negative.

$$3\,H_{2\ (g)} + N_{2\ (g)} \rightleftharpoons 2\,NH_{3\ (g)}$$

with $\Delta G = -16.48\ \frac{kJ}{mol}$

yields

$$2\,H_2O_{(g)} + \cancel{3}\,H_{2\ (g)} + N_{2\ (g)} \rightleftharpoons \cancel{2\,H_{2\ (g)}} + O_{2\ (g)} + 2\,NH_{3\ (g)}$$

with ΔG = $+212.11\ \frac{kJ}{mol}$

Since ΔG is positive, we know the reaction is still not spontaneous after being coupled with a spontaneous reaction

Q35A

A reaction at constant temperature and pressure is spontaneous if $\Delta G < 0$ and nonspontaneous if $\Delta G > 0$. Over what range of temperatures is each of the following processes spontaneous? Assume that all gases are at a pressure of 1 atm. (Hint: Use Tables T1 to calculate ΔH and ΔS (assumed independent of temperature and equal to ΔH° and ΔS°, respectively, and then use the definition of ΔG).

a. Photosynthesis, a reaction of how plants produce food for themselves and animals, and convert carbon dioxide into water:

$$6\,CO_2(g) + 6\,H_2O(l) + \text{light} \longrightarrow C_6H_{12}O_6(s) + 6\,O_2(g)$$

b. The combustion reaction of propane, found in gas grills and some fireplaces:

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l)$$

c. Methane burning in O_2 gas.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$$

Solution

a. First calculate ΔH° and $\Delta S^\circ$of the reaction $6\,CO_2(g) + 6\,H_2O(l) + \text{light} \longrightarrow C_6H_{12}O_6(s) + 6\,O_2(g)$ from the data in Tables T1.

$$\Delta H^\circ = -1273.3 + (6 \times 0) - (6 \times -393.5) - (6 \times -285.8) = 2802.5\ \frac{kJ}{mol}$$

$$\Delta S^\circ = 212.1 + (6 \times 205.2) - (6 \times 213.8) - (6 \times 70) = -259.5\ \frac{J}{mol.\,K}$$

Since the problem asks for the temperature range in which the reaction is spontaneous. The changeover from spontaneity to non-spontaneity occurs at $\Delta G^\circ = 0$. To find the temperature the makes $\Delta G^\circ = 0$, the relationship of $\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$ will be used. Remember to convert ΔS° to $kJ\ mol^{-1}$ (or ΔH° to $J\ mol^{-1}$) so that the units cancel out properly.

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{2802.5\ \frac{kJ}{mol}}{0.2595\ \frac{kJ}{mol.\,K}} = 10799.6\ K$$

Because ΔH° and ΔS° are both positive, the reaction is spontaneous at temperatures above 10799.6 K.

Reviewer Note: The solution is incorrect here. Because $\Delta H^\circ > 0$ and $\Delta S^\circ < 0$, the reaction is never spontaneous.

b. Perform similar calculations for the reaction $C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l)$

$$\Delta H^\circ = (3 \times -393.5) + (4 \times -285.83) + 103.8 - (5 \times 0) = -2220.02\ \frac{kJ}{mol}$$

$$\Delta S^\circ = (3 \times 28) + (4 \times 70) - 270.3 - (5 \times 205.2) = -374.9\ \frac{J}{mol.\,K}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{2220.02\ \frac{kJ}{mol}}{0.3749\ \frac{kJ}{mol.\,K}} = 5922\ K$$

Since ΔH° and ΔS° are both negative, the reaction is spontaneous below 5922 K.

c. The reaction $CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$

$$\Delta H^\circ = (-393.5) + (2 \times -285.8) + 74.6 - (2 \times 0) = -890.5\ \frac{kJ}{mol}$$

$$\Delta S^\circ = (28) + (2 \times 70) - 186.3 - (2 \times 205.2) = -242.9\ \frac{J}{mol.\,K}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-890.5\ \frac{kJ}{mol}}{-0.2429\ \frac{kJ}{mol.\,K}} = 3666\ K$$

Since ΔH° and ΔS° are both negative, the reaction is spontaneous below 3666 K.

Q35B

Over what temperatures are these reactions spontaneous (under constant pressure and temperature)? You may need to use Table 1.

a. $\mathrm{S(s, rhombic) + Zn(s) \rightarrow ZnS(s, sphalerite)}$
b. $\mathrm{2\,Cu(s) + Cl_2 \rightarrow 2\,CuCl(s)}$
c. $\mathrm{4\,Al(s) + 3\,O_2(g) \rightarrow 2\,Al_2O_3(s)}$

Answer

By calculating ΔH_{rxn} and ΔS_{rxn} un der standard conditions and at 25$^\mathrm{o}$C, we can calculate the range of temperature in which ΔG is positive and therefore spontaneous. To calculate ΔH_{rxn} and ΔS_{rxn}, we use Hess's Law , in which:

$$\Delta H_{rxn} = \sum nH_{products} - \sum nH_{reactants}$$

$$\Delta S_{rxn} = \sum nS_{products} - \sum nS_{reactants}$$

a)

$$\mathrm{\Delta H_{rxn} = -206.0 \text{–} (0 + 0) = -206.0\frac{kJ}{mol}}$$

$$\mathrm{\Delta S_{rxn} = 57.7 \text{–} (41.6 + 32.1) = -16\frac{J}{K.\,mol}}$$

$$\mathrm{\Delta G_{rxn} = -206.0 - T(-0.016)}$$

From here, we can set T = 0 because we know that ΔG must be < 0 to be a spontaneous reaction.

T<12875K

b)

$$\mathrm{\Delta H_{rxn} = (2 \times -137.2) \text{–} (0 + 0) = -274.4\frac{kJ}{mol}}$$

$$\Delta S_{rxn} = (2\times 86.2) - ((2\times 33.2) + 223.1) = -117.1 \frac{J}{K.mol}$$

$$\Delta G_{rxn} = -274.4 - T(-0.1171)$$

T < 2343.3K

c)

$$\Delta H_{rxn} = (2(-1675.7)) - (0+0) = -3351.4 \frac{kJ}{mol}$$

$$\Delta S_{rxn} = (2(50.92) - (4(28.3) + (3(205.2)) = -626.96 \frac{J}{K.mol}$$

$$\Delta G_{rxn} = -3351.4 - T(-0.62696)$$

T < 5345.5K

Q37

Determine if the following reaction is spontaneous at 25°C by evaluating $\Delta H°_{rxn}$, $\Delta S°_{rxn}$ and $\Delta G°_{rxn.}$

$$N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2\,H_2O(l)$$

Solution

- $\Delta H^{\circ}_{rxn} = 0 + (2\times -285.8) - 0 - 50.6 = 622.2 \frac{kJ}{mol}$
- $\Delta S^{\circ}_{rxn} = (2\times 70.0) + 191.6 - 205.2 - 121.2 = 5.2 \frac{J}{mol.K}$
- $\Delta G^{\circ}_{rxn} = -622.2 - (25 + 273.15)(0.0052) = -623.8 \frac{kJ}{mol}$

=> Spontaneous ($\Delta G^{\circ}_{rxn} < 0$)

Q39

A thermodynamic engine operates cyclically and reversibly between two temperatures reservoirs, absorbing heat from the high-temperature bath at 600 K and discarding heat to low-temperature bath at 300 K.

a. What is the thermodynamic efficiency of the engine?
b. How much heat is absorbed from the high-temperature bath if -1800 J of heat is discarded to the low-temperature bath during each cycle?
c. How much work does the engine perform in one cycle of operation?

Solution

(a)

$$\text{Thermodynamic efficiency} = \frac{(T_1 - T_2)}{T_1}$$

$$\frac{(600\text{ K} - 300\text{ K})}{(600\text{ K})} \times 100\% = 50\%$$

(b)

$$\frac{1800\text{ J}}{50\%} = 3600\text{ J}$$

(c)

$$-3600\text{ J} \times 50\% = -1800\text{ J}$$

Q41

Acetone (C_3H_6O) is an volatile liquid with a normal boiling point of 56°C and a molar enthalpy of vaporization of 29.1 kJ mol^{-1}. What is the molar entropy of vaporization of acetone under 1 atm of pressure?

Solution

First we need the write the equation relating entropy and enthalpy:

$$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}$$

As a result of the process of normal boiling being at quilibrium $\Delta G = 0$ so all that needs to be done is T in Kelvin and ΔH_{vap} needs to be plugged in and then we solve for ΔS_{vap}:

$$0 = 29.1\ \frac{\text{kJ}}{\text{mol}} - (329\text{ K})(\Delta \text{S}_{\text{vap}})$$

$$\Delta \text{S}_{\text{vap}} = 88.45 \frac{\text{J}}{\text{K. mol}}$$

Q53

Under standard conditions and 25°C, you have this reversible process

$$\text{Sn(s, white)} \longrightarrow \text{Sn(s, gray)}$$

a. Is the change in entropy (ΔS) for this reaction positive or negative? Calculate the change in entropy using Table T1.
b. Calculate (ΔS) for the reaction if ΔH for this reaction is -2.1 kJ/mol.

Solution

For part a), we use the formula

$$\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum nS^\circ(\text{reactants})$$

Plugging in the values from Table T1 gives us

$$\Delta S = 44.1 - 55.2 = -7.1 \frac{J}{mol \cdot K}$$

For part b), we use the formula for a reversible process

$$\Delta S = \frac{\Delta H}{T}$$

$\Delta S = \frac{-2100\ \ J/mol}{298.15\ \ K}$

$\Delta S = -7.04 \frac{J}{mol \cdot K}$

Q59

Compute the ΔG°_f for the following reaction the reaction. The ΔG°_f of H_2SO_3 (aq) is -537.81 kJ mol^{-1}, the ΔG°_f of SO_2 (g) is -300.19 kJ mol^{-1}, and the ΔG°_f of H_2O (g) is -120.42 kJ mol^{-1}.

$$\text{H}_2\text{SO}_3(\text{aq}) \longrightarrow \text{H}_2\text{O(g)} + \text{SO}_2(\text{g})$$

Solution

ΔG° for the reaction is equal to the sum of the G_f° for the products minus the sum of the G_f° for the reactants.

$$\Delta G^\circ = \left(-300.19 \frac{kJ}{mol} + -120.42 \frac{kJ}{mol}\right) - \left(-537.81 \frac{kJ}{mol}\right)$$

$$\Delta G^\circ = 117.2 \frac{kJ}{mol}$$

Q61

Professor Nesral wants to create some water through the combustion of hydrogen. This reaction is depicted as follows:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$$

Is this reaction spontaneous? Prove it by calculating ΔG° at 298.15K. Suppose that Nesral asks his friend in El Azizia, Libya, where the temperature is around $57^{\circ}C$ (330K), to perform the same reaction. Calculate the Gibbs energy for this value and compare it to ΔG°.

Relevant Information:

Entropy Values (S°; $\frac{J}{mol\,K}$)

- Hydrogen: 130.6
- Water: 188.7
- Oxygen: 205.6

Enthalpy Values(H°; $\frac{kJ}{mol}$)

- ΔH_f° Water: -241.826

Solution

From intuition, the equation shows that 3 moles of gas, 2 moles of H_2 and 1 mole of O_2, are reacting to form 2 moles of H_2O gas. This is a decrease in entropy, which may hint at the reaction being non spontaneous. ΔG° should still be calculated to make sure.

The information provided is the entropic values of the product and reactants, and the enthalpy of water. If the ΔS° is calculated, then the ΔG° can also be found using the following equation:

$$\Delta G = \Delta H^{\circ}_{rxn} - T\Delta S^{\circ}_{rxn}.$$

Where ΔH°_{rxn} is the Heat and ΔS°_{rxn} is the entropy of the reaction under standard conditions (constant pressure), and T is temperature. Knowing that ΔS°_{rxn} is a state variable, it can be calculated as the difference between the sum of the entropy values of the products and reactants multiplied by their coefficients (This is known as Hess's Law). In other words,

$$\Delta S^{\circ} = \sum n_{products} \times S^{\circ}_{f_{products}} - \sum n_{reactants} \times S^{\circ}_{f_{reactants}}$$

From this, ΔS°_{rxn} can be calculated as such:

$$\Delta S^{\circ} = \left(2 \times 188.7 \frac{J}{molK}\right) - \left(\left[2 \times 130.6 \frac{J}{molK}\right] + \left[205.6 \frac{J}{molK}\right]\right)$$

$$= -89.4 \frac{J}{mol.\,K}$$

Since both H_2 and O_2 are in their natural states, the H_f° associated with them equals to zero. Since enthalpy (ΔH°_{rxn}) is also a state variable, it can be calculated with Hess's Law as well.

$$\Delta H^{\circ} = \left(2 \times -241.826 \frac{kJ}{mol}\right) - \left(\left[0 \frac{kJ}{mol}\right] + \left[0 \frac{kJ}{mol}\right]\right)$$

$$\Delta H^{\circ} = -483.652 \frac{kJ}{mol}$$

Plugging in these values, as well as the temperature, $298.15K$, will yield ΔG°.

$$\Delta G^{\circ}_{rxn} = \Delta H^{\circ}_{rxn} - T\Delta S^{\circ}_{rxn}.$$

$$\Delta G^{\circ}_{rxn} = -483.652 \frac{kJ}{mol} - 298.15K \left(-0.0894 \frac{kJ}{mol.\,K}.\right)$$

$$\Delta G^{\circ}_{rxn} = -456.99739 \frac{kJ}{mol}$$

The ΔG_{rxn} is therefore $-456.99739 \frac{kJ}{mol}$ This very negative value means that the reaction is DEFINITELY spontaneous. It also makes sense on a conceptual level because combustion reaction like these release a lot of heat, which means that the process if enthalpically driven! Calculating the ΔG_{rxn} at a different temperature, as mentioned in the problem, has the same method:

$\Delta G_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$.

$\Delta G_{rxn} = -483.652 \frac{kJ}{mol} - 330K \left(-0.0894 \frac{kJ}{mol.K}.\right)$

$\Delta G_{rxn} = -454.15 \frac{kJ}{mol}$

In both situations the ΔG_{rxn} is very negative, but in the hotter climate it is slightly less so. What this shows is that, at a higher temperatures the entropic factors contribute more to the gibbs energy than at standard conditions. This showcases the temperature dependence of entropy. In another reaction that released less energy, this difference may have made the reaction non-spontaneous!

Abstract : Hess's Law to find ΔG_{rxn}.

Q63A

The concentration of sodium in the plasma is approximately 0.14 M. While in the fluid outside of the plasma, sodium concentration is about 0.5 M.

a. In what direction will the sodium ions spontaneously move past the cell wall?
b. The spontaneous process of movement in part a is called "passive transport". Movement in the opposite direction is called "active transport" and requires work to happen. Calculate the amount of free energy required to move 5 moles of Na^+ by active transport (non-spontaneous direction) at 273 K.

Solution

a) The Na^+ ions will spontaneously flow into the plasma because it flows from high to low concentration.

b) $\Delta G = nRT \ln \frac{c_2}{c_1}$ where c_2 is the destination of Na^+ after active transport occurs while c_1 is the original concentration of the Na^+ ions.

$\Delta G = (5 \text{ mole})(8.3145 \frac{J}{K.mol})(273 \text{ K}) \ln \frac{0.5}{0.14}$

$\Delta G = 14447.26 \text{ J}$

Q63B

For a hypothetical nerve cell, the sodium ion concentration is 0.015 M outside the cell and 0.00045 M inside the cell. Active transport involves using proteins and chemical energy stored in ATP to move the ions in a thermodynamically unfavorable direction. Assuming that conditions in the cell allow the hydrolysis of a single ATP molecule to give 2.05×10^{-18} J of usable enegy. How many molecules of ATP would be needed to move 0.005 moles of sodium ions using active transport at standard conditions? You can assume that the sodium ion concentrations remain constant.

Solution

To answer this question, the change of free energy is needed which means the following equation is needed

$$\Delta G = -RTlnQ$$

$$R = 8.314 \frac{J}{mol.K} \qquad T = 298K \qquad Q = \frac{[Na^+]_{in}}{[Na^+]_{out}}$$

$$\Delta G = -8.314 \frac{J}{mol.K} \times 298K \times ln(\frac{0.00045\ M}{0.015\ M})$$

$$\Delta G = -2424\ \frac{J}{mol} \times ln(0.03) = 8688\ \frac{J}{mol}$$

Now that we have the the free energy, we can determine the number of ATP molecules needed

$$8688\ \frac{J}{mol} \times 0.005\ mol = 43.4\ J$$

$$\frac{43.4\ J}{2.05 \times 10^{-18}\ J\ molecule^{-1}} = 2.119 \times 10^{19}\ \text{ ATP molecules}$$

Answer: $2.119 \times 10^{19}\ \text{ ATP molecules}$

CHAPTER OVERVIEW

14: Chemical Equilibrium

An General Chemistry Libretexts Textmap organized around the textbook
Principles of Modern Chemistry
by Oxtoby, Gillis, and Campion

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI
XVII XVIII XIX XX XXI XXII XXIII • **Homework Exercises**

Template:HideTOC

Chemical equilibrium is the state in which both reactants and products are present in concentrations which have no further tendency to change with time. This results when the forward reaction proceeds at the same rate as the reverse reaction. Thus, no net changes in the concentrations of the reactant(s) and product(s) are observed. This is known as dynamic equilibrium.

14.1: The Nature of Chemical Equilibrium

Learning Objectives

- To understand what is meant by chemical equilibrium.

In the last chapter, we discussed the principles of chemical kinetics, which deal with the *rate of change*, or how quickly a given chemical reaction occurs. We now turn our attention to the *extent* to which a reaction occurs and how reaction conditions affect the final concentrations of reactants and products. For most of the reactions that we have discussed so far, you may have assumed that once reactants are converted to products, they are likely to remain that way. In fact, however, virtually all chemical reactions are *reversible* to some extent. That is, an opposing reaction occurs in which the products react, to a greater or lesser degree, to re-form the reactants. Eventually, the forward and reverse reaction rates become the same, and the system reaches **chemical equilibrium,** the point at which the composition of the system no longer changes with time.

Figure 14.1.1: Dinitrogen tetroxide is a powerful oxidizer that reacts spontaneously upon contact with various forms of hydrazine, which makes the pair a popular propellant combination for rockets. Nitrogen dioxide at −196 °C, 0 °C, 23 °C, 35 °C, and 50 °C. (NO_2) converts to the colorless dinitrogen tetroxide (N_2O_4) at low temperatures, and reverts to NO_2 at higher temperatures. (CC BY-SA 3.0; Eframgoldberg).

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide (N_2O_4) to nitrogen dioxide (NO_2). You may recall that NO_2 is responsible for the brown color we associate with smog. When a sealed tube containing solid N_2O_4 (mp = −9.3°C; bp = 21.2°C) is heated from −78.4°C to 25°C, the red-brown color of NO_2 appears (Figure 14.1.1). The reaction can be followed visually because the product (NO_2) is colored, whereas the reactant (N_2O_4) is colorless:

$$\underset{colorless}{N_2O_4(g)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \underset{red-brown}{2\,NO_2(g)} \tag{14.1.1}$$

The double arrow indicates that both the forward reaction

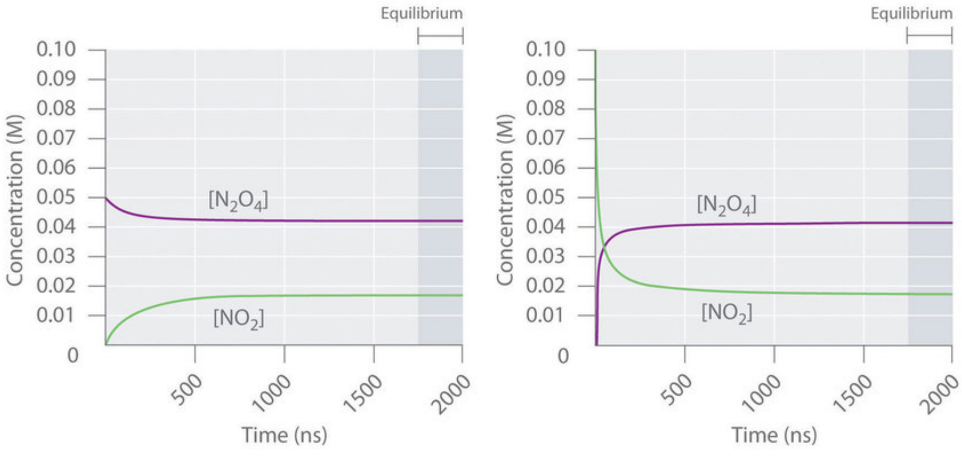
$$N_2O_4(g) \xrightarrow{k_f} 2\,NO_2(g) \tag{14.1.2}$$

and reverse reaction

$$2\,NO_2(g) \xrightarrow{k_r} N_2O_4(g) \tag{14.1.3}$$

occurring simultaneously (i.e, the reaction is reversible). However, this does not necessarily mean the system is equilibrium as the following chapter demonstrates.

Figure 14.1.2 shows how the composition of this system would vary as a function of time at a constant temperature. If the initial concentration of NO_2 were zero, then it increases as the concentration of N_2O_4 decreases. Eventually the composition of the system stops changing with time, and chemical equilibrium is achieved. Conversely, if we start with a sample that contains no N_2O_4 but an initial NO_2 concentration twice the initial concentration of N_2O_4 (Figure 14.1.2*a*), in accordance with the stoichiometry of the reaction, we reach exactly the same equilibrium composition (Figure 14.1.2b). Thus equilibrium can be approached from either direction in a chemical reaction.



(a) **(b)**

Figure 14.1.2: The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system contains 0.1000 M NO_2 and no N_2O_4. The concentration of NO_2 decreases with time as the concentration of N_2O_4 increases. In both cases, the final concentrations of the substances are the same: [N_2O_4] = 0.0422 M and [NO_2] = 0.0156 M at equilibrium. (CC BY-SA-NC; Anonymous by request)

Figure 14.1.3 shows the forward and reverse reaction rates for a sample that initially contains pure NO_2. Because the initial concentration of N_2O_4 is zero, the forward reaction rate (dissociation of N_2O_4) is initially zero as well. In contrast, the reverse reaction rate (dimerization of NO_2) is initially very high ($2.0 \times 10^6\ M/s$), but it decreases rapidly as the concentration of NO_2 decreases. As the concentration of N_2O_4 increases, the rate of dissociation of N_2O_4 increases—but more slowly than the dimerization of NO_2—because the reaction is only first order in N_2O_4 (rate = $k_f[N_2O_4]$, where k_f is the rate constant for the forward reaction in Equations 14.1.1 and 14.1.2). Eventually, the forward and reverse reaction rates become identical, $k_f = k_r$, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at different rates, then the system is not at equilibrium.

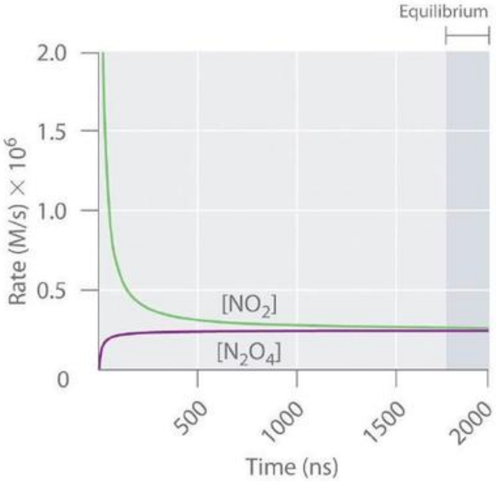


Figure 14.1.3: The Forward and Reverse Reaction Rates as a Function of Time for the $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ System Shown in Part (b) in Figure 14.1.2. (CC BY-SA-NC; Anonymous by request)

The rate of dimerization of NO_2 (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of N_2O_4 is zero, the rate of the dissociation reaction (forward reaction) at $t = 0$ is also zero. As the dimerization reaction proceeds, the N_2O_4 concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of N_2O_4 and NO_2 no longer change.

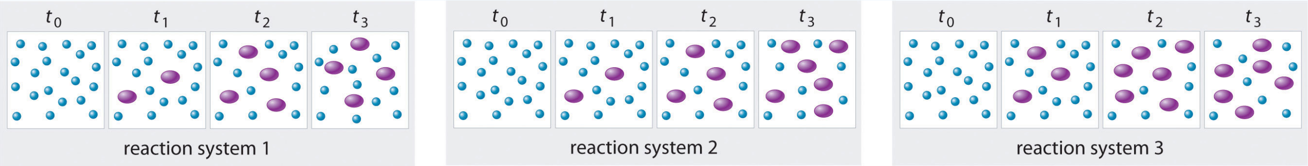
> *At equilibrium, the forward reaction rate is equal to the reverse reaction rate.*

Example 14.1.1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation:

$$2A \rightleftharpoons B$$

where the blue circles are A and the purple ovals are B. Each set of panels shows the changing composition of one of the three reaction mixtures as a function of time. Which system took the longest to reach chemical equilibrium?



In reaction system 1 theree are four purple ovals at t3. In reaction system 2 there are size purple ovals at t3. In reaction system systems there are six ovals at t2 and t3.

Given: three reaction systems

Asked for: relative time to reach chemical equilibrium

Strategy:

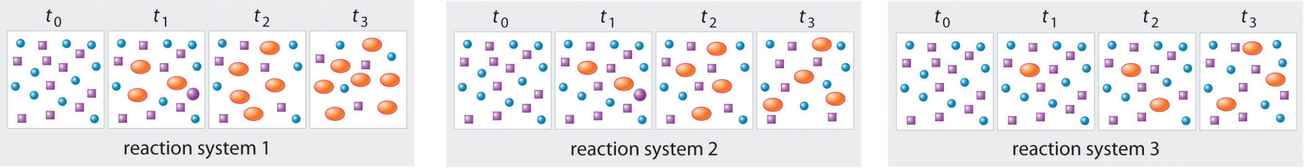
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

Solution:

In systems 1 and 3, the concentration of A decreases from t_0 through t_2 but is the same at both t_2 and t_3. Thus systems 1 and 3 are at equilibrium by t_3. In system 2, the concentrations of A and B are still changing between t_2 and t_3, so system 2 may not yet have reached equilibrium by t_3. Thus system 2 took the longest to reach chemical equilibrium.

Exercise 14.1.1

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B ⇌ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?



In reaction system 1 there are seven orange ovals at t3. In reaction system two there are four orange ovals at t3. In reaction system three there are three orange ovals at t3.

Answer

system 2

A Video Introduction to Dynamic Equilibrium: Introduction to Dynamic Equilibrium(opens in new window) [youtu.be]

Summary

At equilibrium, the forward and reverse reactions of a system proceed at equal rates. Chemical equilibrium is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

14.2: The Empirical Law of Mass Action

Learning Objectives

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.
- To understand how different phases affect equilibria.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the decomposition reaction of N_2O_4 to NO_2. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[N_2O_4] \tag{14.2.1}$$

and

$$\text{reverse rate} = k_r[NO_2]^2 \tag{14.2.2}$$

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

$$k_f[N_2O_4] = k_r[NO_2]^2 \tag{14.2.3}$$

so

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]} \tag{14.2.4}$$

The ratio of the rate constants gives us a new constant, the **equilibrium constant** (K), which is defined as follows:

$$K = \frac{k_f}{k_r} \tag{14.2.5}$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.

> The equilibrium constant is equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction.

Table $14.2.1$ lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 14.2.1. At equilibrium the magnitude of the quantity $[NO_2]^2/[N_2O_4]$ is essentially the same for all five experiments. In fact, no matter what the initial concentrations of NO_2 and N_2O_4 are, at equilibrium the quantity $[NO_2]^2/[N_2O_4]$ will always be $6.53 \pm 0.03 \times 10^{-3}$ at 25°C, which corresponds to the ratio of the rate constants for the forward and reverse reactions (Equation 14.2.5). That is, at a given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of the reactants and products vary depending on their initial concentrations.

Table 14.2.1: Initial and Equilibrium Concentrations for $NO_2 : N_2O_4$ Mixtures at 25°C

	Initial Concentrations		Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
1	0.0500	0.0000	0.0417	0.0165	6.54×10^{-3}
2	0.0000	0.1000	0.0417	0.0165	6.54×10^{-3}
3	0.0750	0.0000	0.0647	0.0206	6.56×10^{-3}
4	0.0000	0.0750	0.0304	0.0141	6.54×10^{-3}

	Initial Concentrations		Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
5	0.0250	0.0750	0.0532	0.0186	6.50×10^{-3}

Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction of the general form

$$aA + bB \rightleftharpoons cC + dD \tag{14.2.6}$$

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{14.2.7}$$

where K is the equilibrium constant for the reaction. Equation 14.2.6 is called the equilibrium equation, and the right side of Equation 14.2.7 is called the equilibrium constant expression. The relationship shown in Equation 14.2.7 is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of K shown in Table 14.2.2, for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reductant and Cl_2 is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of K less than 10^{-3} indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

Table 14.2.2: Equilibrium Constants for Selected Reactions*

Reaction	Temperature (K)	Equilibrium Constant (K)
$S(s) + O_2(g) \rightleftharpoons SO_2(g)$	300	4.4×10^{53}
$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g)$	500	2.4×10^{47}
$H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g)$	300	1.6×10^{33}
$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$	300	4.1×10^{18}
$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$	300	4.2×10^{13}
$3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$	300	2.7×10^{8}
$H_2(g) + D_2(g) \rightleftharpoons 2\,HD(g)$	100	1.92
$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$	300	2.9×10^{-1}
$I_2(g) \rightleftharpoons 2\,I(g)$	800	4.6×10^{-7}
$Br_2(g) \rightleftharpoons 2\,Br(g)$	1000	4.0×10^{-7}
$Cl_2(g) \rightleftharpoons 2\,Cl(g)$	1000	1.8×10^{-9}
$F_2(g) \rightleftharpoons 2\,F(g)$	500	7.4×10^{-13}

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.

You will also notice in Table 14.2.2 that equilibrium constants have no units, even though Equation 14.2.7 suggests that the units of concentration might not always cancel because the exponents may vary. **In fact, equilibrium constants are calculated using "effective concentrations," or activities, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M.** As shown in Equation 14.2.8, the units of concentration cancel, which makes K unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{mol}{\cancel{L}}}{\frac{mol}{\cancel{L}}} \tag{14.2.8}$$

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

$$H_2(g) + D_2(g) \rightleftharpoons 2\,HD(g) \tag{14.2.9}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]} \tag{14.2.10}$$

with K varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of H_2, D_2, and HD contains significant concentrations of both product and reactants.

Figure 14.2.1 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants \rightleftharpoons products. Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equations 14.2.8 and 14.2.7), when $k_f \gg k_r$, K is a **large** number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f \ll k_r$, K is a very **small** number, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium.

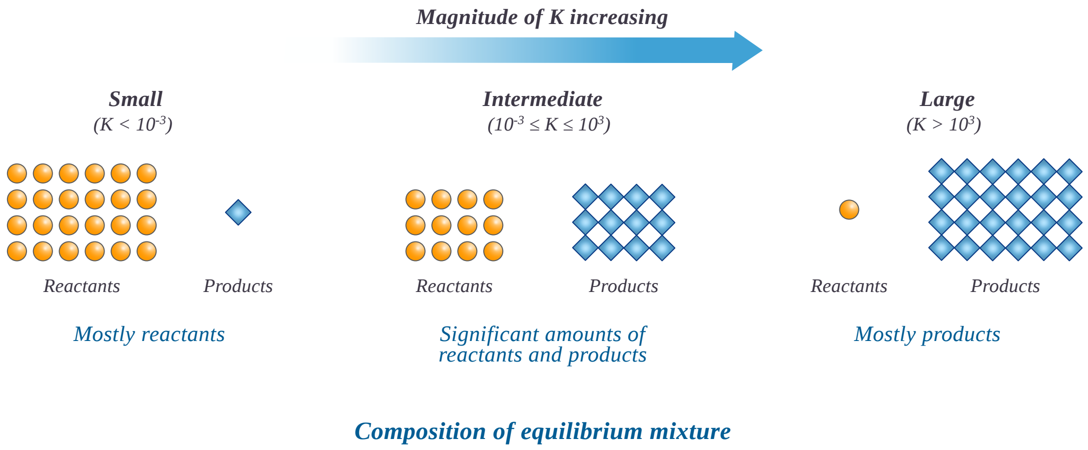


Figure 14.2.1: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium. (CC BY-NC; Ümit Kaya)

> A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.

Example 14.2.1

Write the equilibrium constant expression for each reaction.

- $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$
- $CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$
- $2\,CO_2(g) \rightleftharpoons 2\,CO(g)^{+}O_2(g)$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 14.2.7. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

The only product is ammonia, which has a coefficient of 2. For the reactants, N_2 has a coefficient of 1 and H_2 has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[NH_3]^2}{[N_2][H_2]^3}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and O_2, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[CO_2]}{[CO][O_2]^{1/2}}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for O_2. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2:

$$\frac{[CO]^2[O_2]}{[CO_2]^2}$$

Exercise 14.2.1

Write the equilibrium constant expression for each reaction.

a. $N_2O(g) \rightleftharpoons N_2(g) + \frac{1}{2}O_2(g)$
b. $2\,C_8H_{18}(g) + 25\,O_2(g) \rightleftharpoons 16\,CO_2(g) + 18\,H_2O(g)$
c. $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$

Answer a

$$K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$$

Answer b

$$K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$$

Answer c

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

Example 14.2.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Given: systems and values of K

Asked for: composition of systems at equilibrium

Strategy:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

a. Only system 4 has $K >> 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K << 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise 14.2.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25^\circ C} = 3.3 \times 10^8$,
- $K_{177^\circ C} = 2.6 \times 10^3$, and
- $K_{327^\circ C} = 4.1$.

a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
b. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer a

327°C, where K is smallest

Answer b

25°C

Variations in the Form of the Equilibrium Constant Expression

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 14.2.6 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{14.2.11}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \tag{14.2.12}$$

This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is as follows:

$$K = \frac{[NO_2]^2}{[N_2O_4]} \tag{14.2.13}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K′ is given by the inverse expression:

$$K' = \frac{[N_2O_4]}{[NO_2]^2} \tag{14.2.14}$$

Consider another example, the formation of water: $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$. Because H_2 is a good reductant and O_2 is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form O_2 and H_2, is very small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into H_2 and O_2.

> The equilibrium constant for a reaction written in reverse is the *inverse* of the equilibrium constant for the reaction as written originally.

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, we could write the equation for the reaction

$$2NO_2 \rightleftharpoons N_2O_4 \tag{14.2.15}$$

as

$$NO_2 \rightleftharpoons \frac{1}{2}N_2O_4 \tag{14.2.16}$$

with the equilibrium constant K″ is as follows:

$$K'' = \frac{[N_2O_4]^{1/2}}{[NO_2]} \tag{14.2.17}$$

The values for K′ (Equation 14.2.14) and K″ are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{14.2.18}$$

In general, if all the coefficients in a balanced chemical equation were subsequently multiplied by n, then the new equilibrium constant is the original equilibrium constant raised to the n^{th} power.

✓ Example 14.2.3: The Haber Process

At 745 K, K is 0.118 for the following reaction:

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)}$$

What is the equilibrium constant for each related reaction at 745 K?

a. $\mathrm{2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)}$
b. $\mathrm{\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)}$

Given: balanced equilibrium equation, K at a given temperature, and equations of related reactions

Asked for: values of K for related reactions

Strategy:

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate K for each reaction.

Solution:

The equilibrium constant expression for the given reaction of $\mathrm{N_2(g)}$ with $\mathrm{H_2(g)}$ to produce $\mathrm{NH_3(g)}$ at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118$$

This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47$$

In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344$$

? Exercise

At 527°C, the equilibrium constant for the reaction

$$\mathrm{2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)}$$

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$\mathrm{SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g)}$$

Answer

3.6×10^{-3}

Law of Mass Action for Gas-Phase Reactions

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol K_p is used to denote equilibrium constants calculated from partial pressures. For the general reaction

$$\mathrm{aA + bB \rightleftharpoons cC + dD}$$

in which all the components are gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \tag{14.2.19}$$

Thus K_p for the decomposition of N_2O_4 (Equation 14.2.1) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \tag{14.2.20}$$

Like K, K_p is a unitless quantity because the quantity that is actually used to calculate it is an "effective pressure," the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity. The "effective pressure" is called the **fugacity**, just as activity is the effective concentration.

Because partial pressures are usually expressed in atmospheres or mmHg, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, the numerical values of K and K_p are usually different. They are, however, related by the ideal gas constant (R) and the absolute temperature (T):

$$K_p = K(RT)^{\Delta n} \tag{14.2.21}$$

where K is the equilibrium constant expressed in units of concentration and Δn is the difference between the numbers of moles of gaseous products and gaseous reactants ($n_p - n_r$). The temperature is expressed as the absolute temperature in Kelvin. According to Equation 14.2.21, $K_p = K$ only if the moles of gaseous products and gaseous reactants are the same (i.e., $\Delta n = 0$). For the decomposition of N_2O_4, there are 2 mol of gaseous product and 1 mol of gaseous reactant, so $\Delta n = 1$. Thus, for this reaction,

$$K_p = K(RT)^1 = KRT \tag{14.2.22}$$

✓ Example 14.2.4: The Haber Process (again)

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

What is K_p for this reaction at the same temperature?

Given: equilibrium equation, equilibrium constant, and temperature

Asked for: K_p

Strategy:

Use the coefficients in the balanced chemical equation to calculate Δn. Then use Equation 14.2.21to calculate K from K_p.

Solution:

This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2-4) = -2$. We know K, and $T = 745\ K$. Thus, from Equation 14.2.18, we have the following:

$$K_p = K(RT)^{-2} = \frac{K}{(RT)^2} = \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2} = 3.16 \times 10^{-5}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

? Exercise 14.2.4:

Calculate K_p for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer

$K_p = 1.2 \times 10^3$

Law of Mass Action for Reactions Involving Pure Substances and Multiple Phases

When the products and reactants of a reaction at equilibrium in a single phase (e.g., liquid, gas or solids of different lattices), the system is a **homogeneous equilibrium**. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system where the reactants and products are in two or more phase is called a **heterogeneous equilibrium** (e.g, the reaction of a gas with a solid or liquid or two different solid lattices in co-existing).

Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, their concentrations are treated as constants, which allows us to simplify equilibrium constant expressions that involve pure solids or liquids.The reference states for pure solids and liquids are those forms stable at 1 bar (approximately 1 atm), which are assigned an activity of 1. (Recall that the density of water, and thus its volume, changes by only a few percentage points between 0 °C and 100 °C.)

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$\mathrm{CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)} \tag{14.2.23}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K=\frac{[CO]^2}{[CO_2][C]} \tag{14.2.24}$$

Because graphite is a solid, however, its molar concentration, determined from its density and molar mass, is essentially constant and has the following value:

$$[C]=\frac{2.26\ \cancel{g}/\ \cancel{cm^3}}{12.01\ \ \cancel{g}/mol}\times 1000\ \ \cancel{cm^3}/L=188\ mol/L=188\ M \tag{14.2.25}$$

We can rearrange Equation 14.2.25so that the constant terms are on one side:

$$K[C]=K(188)=\frac{[CO]^2}{[CO_2]} \tag{14.2.26}$$

Incorporating the constant value of $[C]$ into the equilibrium equation for the reaction in Equation 14.2.26,

$$K'=\frac{[CO]^2}{[CO_2]} \tag{14.2.27}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p=\frac{(P_{CO})^2}{P_{CO_2}} \tag{14.2.28}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the concentrations of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and CO_2, the system described in Equation 14.2.23will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 14.2.2, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

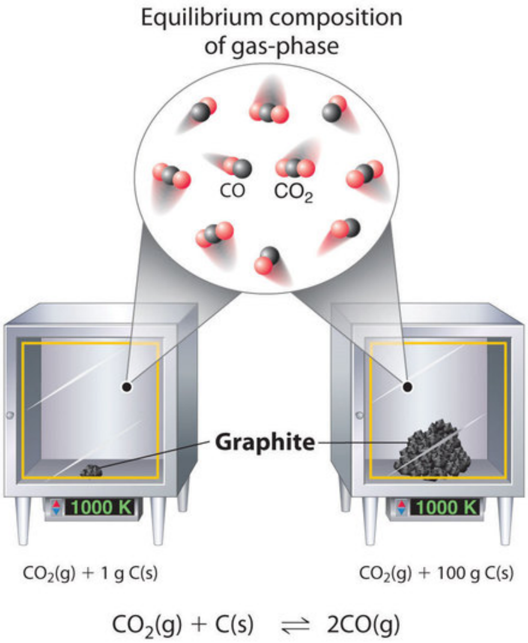


Figure 14.2.2: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

Example 14.2.1

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

a. $PCl_{3(l)} + Cl_{2(g)} \rightleftharpoons PCl_{5(s)}$
b. $Fe_3O_{4(s)} + 4H_{2(g)} \rightleftharpoons 3Fe_{(s)} + 4H_2O_{(g)}$

Given: balanced equilibrium equations

Asked for: expressions for K and K_p

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution

This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their concentrations do not appear in the equilibrium constant expression because they do not change significantly. So

$$K = \frac{1}{[Cl_2]}$$

and

$$K_p = \frac{1}{P_{Cl_2}}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which do not appear in the equilibrium constant expressions. The two gases do, however, appear in the expressions:

$$K = \frac{[H_2O]^4}{[H_2]^4}$$

and

$$K_p = \frac{(P_{H_2O})^4}{(P_{H_2})^4}$$

Exercise 14.2.1

Write the expressions for K and K_p for the following reactions.

a. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
b. $\underbrace{C_6H_{12}O_{6(s)}}_{glucose} + 6O_{2(g)} \rightleftharpoons 6CO_{2(g)} + 6H_2O_{(g)}$

Answer a

$K = [CO_2]$ and $K_p = P_{CO_2}$

Answer b

$$K = \frac{[CO_2]^6[H_2O]^6}{[O_2]^6} \text{ and } K_p = \frac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$$

For reactions carried out in solution, the concentration of the solvent is omitted from the equilibrium constant expression even when the solvent appears in the balanced chemical equation for the reaction. The concentration of the solvent is also typically much greater than the concentration of the reactants or products (recall that pure water is about 55.5 M, and pure ethanol is about 17 M). Consequently, the solvent concentration is essentially constant during chemical reactions, and the solvent is therefore treated as a pure liquid. The equilibrium constant expression for a reaction contains only those species whose concentrations could change significantly during the reaction.

> The concentrations of pure solids, pure liquids, and solvents are omitted from equilibrium constant expressions because they do not change significantly during reactions when enough is present to reach equilibrium.

Summary

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.
- Definition of equilibrium constant in terms of forward and reverse rate constants:

$$K = \frac{k_f}{k_r}$$

- Equilibrium constant expression (law of mass action):

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Equilibrium constant expression for reactions involving gases using partial pressures:

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

- Relationship between K_p and K:

$$K_p = K(RT)^{\Delta n}$$

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the equilibrium constant (K), a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same K. For a system at equilibrium, the law of mass action relates K to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the equilibrium equation. The ratio is called the equilibrium constant expression. When a reaction is written in the reverse direction, K and the equilibrium constant expression are inverted. For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures (K_p) is related to K by the ideal gas constant (R), the temperature (T), and the change in the number of moles of gas during the reaction. An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

14.3: Thermodynamic Description of the Equilibrium State

Learning Objectives

- Gibbs Energy is a state function defined as $G = H - TS$.
- The practical utility of the Gibbs function is that ΔG for any process is negative if it leads to an increase in the entropy of the world. Thus spontaneous change at a given temperature and pressure can only occur when it would lead to a decrease in G.
- The sign of the standard free energy change ΔG^o of a chemical reaction determines whether the reaction will tend to proceed in the forward or reverse direction.
- Similarly, the relative signs of ΔH^o and ΔH^o determine whether the spontaneity of a chemical reaction will be affected by the temperature, and if so, in what way.
- The existence of sharp melting and boiling points reflects the differing temperature dependancies of the free energies of the solid, liquid, and vapor phases of a pure substance, which are in turn reflect their differing entropies.

Previously, we saw that it is the **sum** of the entropy changes of the system and surroundings that determines whether a process will occur spontaneously. In chemical thermodynamics we prefer to focus our attention on the system rather than the surroundings, and would like to avoid having to calculate the entropy change of the surroundings explicitly.

In this unit we introduce a new thermodynamic function, the *free energy*, which turns out to be the single most useful criterion for predicting the direction of a chemical reaction and the composition of the system at equilibrium. However, the term "free energy", although still widely used, is rather misleading, so we will often refer to it as "Gibbs energy." The free energy enables us to do this for changes that occur at a constant temperature and pressure (the *Gibbs energy*) or constant temperature and volume (the *Helmholtz energy*.)

Free energy: the Gibbs function

The Gibbs energy (also known as the *Gibbs function* or *Gibbs Potential*) is defined as

$$G = H - TS \tag{14.3.1}$$

in which S refers to the entropy of the *system*. Since H, T and S are all state functions, so is G. Thus for any change in state (under constant temperature), we can write the extremely important relation

$$\Delta G = \Delta H - T\Delta S \tag{14.3.2}$$

How does this simple equation encompass the entropy change of the world ΔS_{total}, which we already know is the sole criterion for spontaneous change from the second law of thermodynamics? Starting with the definition

$$\Delta S_{total} = \Delta S_{surr} + \Delta S_{sys} \tag{14.3.3}$$

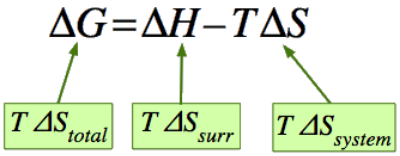
we would first like to get rid of ΔS_{surr}. How can a chemical reaction (a change in the *system*) affect the entropy of the *surroundings*? Because most reactions are either exothermic or endothermic, they are accompanied by a flow of heat q_p across the system boundary. The enthalpy change of the reaction ΔH is defined as the flow of heat into the system from the surroundings when the reaction is carried out at constant pressure, so the heat withdrawn from the surroundings will be $-q_p$ which will cause the entropy of the surroundings to change by $-q_p/T = -\Delta H/T$. We can therefore rewrite Equation 14.3.3 as

$$\Delta S_{total} = \frac{-\Delta H}{T} + \Delta S_{sys} \tag{14.3.4}$$

Multiplying each side by $-T$, we obtain

$$-T\Delta S_{total} = \Delta H - T\Delta S_{sys} \tag{14.3.5}$$

which expresses the entropy change of the world in terms of thermodynamic properties of the *system* exclusively. If $-T\Delta S_{total}$ is denoted by ΔG, then we have Equation 14.3.2 which defines the *Gibbs energy* change for the process.



From the foregoing, you should convince yourself that G will decrease in any process occurring at constant temperature and pressure which is accompanied by an overall increase in the entropy. The constant temperature is a consequence of the temperature and the enthalpy appearing in the preceding Equation 14.3.5. Since most chemical and phase changes of interest to chemists take place under such conditions, the Gibbs energy is the most useful of all the thermodynamic properties of a substance, and (as we shall see in the lesson that follows this one) it is closely linked to the equilibrium constant.

Some textbooks and teachers say that the free energy, and thus the spontaneity of a reaction, depends on both the enthalpy and entropy changes of a reaction, and they sometimes even refer to reactions as "energy driven" or "entropy driven" depending on whether ΔH or the $T\Delta S$ term dominates. This is technically correct, but misleading because it disguises the important fact that ΔS_{total}, which this equation expresses in an indirect way, is the *only* criterion of spontaneous change.

Helmholtz Energy is also a "Free Energy"

We will deal only with the Gibbs energy in this course. The Helmholtz free energy is of interest mainly to chemical engineers (whose industrial-scale processes are often confined to tanks and reactors of fixed volume) and some geochemists whose interest is centered on the chemistry that occurs deep within the earth's surface.

Gibbs Energy and Chemical Change

Remember that ΔG is meaningful only for changes in which the *temperature and pressure remain constant*. These are the conditions under which most reactions are carried out in the laboratory; the system is usually open to the atmosphere (constant pressure) and we begin and end the process at room temperature (after any heat we have added or which is liberated by the reaction has dissipated.) The importance of the Gibbs function can hardly be over-stated: it serves as the single master variable that determines whether a given chemical change is thermodynamically possible. Thus if the free energy of the reactants is greater than that of the products, the entropy of the world will increase when the reaction takes place as written, and so the reaction will tend to take place spontaneously. Conversely, if the free energy of the products exceeds that of the reactants, then the reaction will not take place in the direction written, but it will tend to proceed in the reverse direction.

> *ΔG serves as the single master variable that determines whether a given chemical change is thermodynamically possible. Moreover, it determines the direction and extent of chemical change.*

In a spontaneous change, Gibbs energy always decreases and never increases. This of course reflects the fact that the entropy of the world behaves in the exact opposite way (owing to the negative sign in the $T\Delta S$ term).

$$\mathrm{H_2O(l)} \rightarrow \mathrm{H_2O(s)} \tag{14.3.6}$$

water below its freezing point undergoes a decrease in its entropy, but the heat released into the surroundings more than compensates for this, so the entropy of the world increases, the free energy of the H_2O diminishes, and the process proceeds spontaneously.

> *In a spontaneous change, Gibbs energy **always** decreases and never increases.*

An important consequence of the one-way downward path of the free energy is that once it reaches its minimum possible value, all net change comes to a halt. This, of course, represents the state of chemical equilibrium. These relations are nicely summarized as follows:

- $\Delta G < 0$: reaction can spontaneously proceed to the right:

$$A \rightarrow B$$

- $\Delta G > 0$: reaction can spontaneously proceed to the left:

$$A \leftarrow B$$

- $\Delta G = 0$: the reaction is at **equilibrium** and both $[A]$ and $[B]$ will not change:

$$A \rightleftharpoons B.$$

No need to find the value of ΔG for a Specific Reaction!

This might seem strange, given the key importance ΔG in determining whether or not a reaction will take place in a given direction. It turns out, however, that it is almost never necessary to explicitly evaluate ΔG. As we will show in the lesson that follows this one, it is far more convenient to work with the equilibrium constant of a reaction, within which ΔG is "hidden". This is just as well, because for most reactions (those that take place in solutions or gas mixtures) the value of ΔG depends on the **proportions** of the various reaction components in the mixture; it is not a simple sum of the "products minus reactants" type, as is the case with ΔH.

Recalling the condition for spontaneous change

$$\Delta G = \Delta H - T\Delta S < 0 \tag{14.3.7}$$

it is apparent that the temperature dependence of ΔG depends almost entirely on the entropy change associated with the process. (We say "almost" because the values of ΔH and ΔS are themselves slightly temperature dependent; both gradually increase with temperature). In particular, notice that in the above equation **the sign of the entropy change determines whether the reaction becomes more or less spontaneous as the temperature is raised.** For any given reaction, the sign of ΔH can also be positive or negative. This means that there are four possibilities for the influence that temperature can have on the spontaneity of a process:

Case 1: Δ*H* < 0 and Δ*S* > 0

Both enthalpic ΔH and entropic $-T\Delta S$ terms will be negative, so ΔG will be negative regardless of the temperature. An exothermic reaction whose entropy increases will be spontaneous at all temperatures.

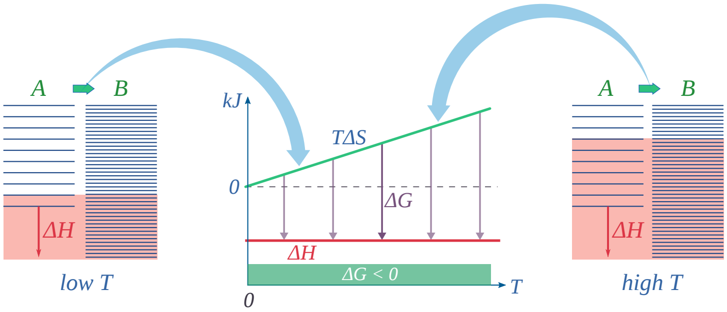


Figure 14.3.1: A hypothetical A ⟶ B reaction that is favored enthalpically and entropically (spontaneous at all temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

Case 2: Δ*H* < 0 and Δ*S* < 0

If the reaction is sufficiently exothermic it can force ΔG negative only at temperatures below which $|T\Delta S| < |\Delta H|$. This means that there is a temperature $T = \Delta H / \Delta S$ at which the reaction is at equilibrium; the reaction will only proceed spontaneously below this temperature. The freezing of a liquid or the condensation of a gas are the most common examples of this condition.

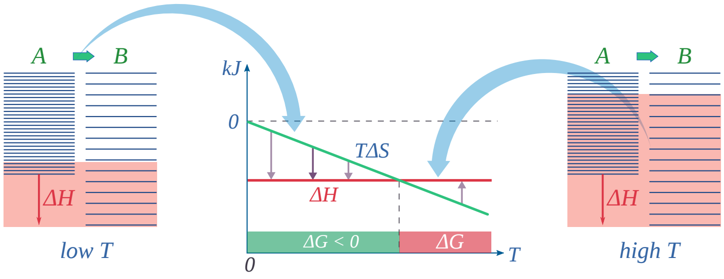


Figure 14.3.2: A hypothetical A $\longrightarrow$ B reaction that is favored enthalpically and is not favored entropically (spontaneous at low temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

Case 3: $\Delta H > 0$ and $\Delta S > 0$

This is the reverse of the previous case; the entropy increase must overcome the handicap of an endothermic process so that $T\Delta S > \Delta H$. Since the effect of the temperature is to "magnify" the influence of a positive ΔS, the process will be spontaneous at temperatures above $T = \Delta H/\Delta S$. (Think of melting and boiling.)

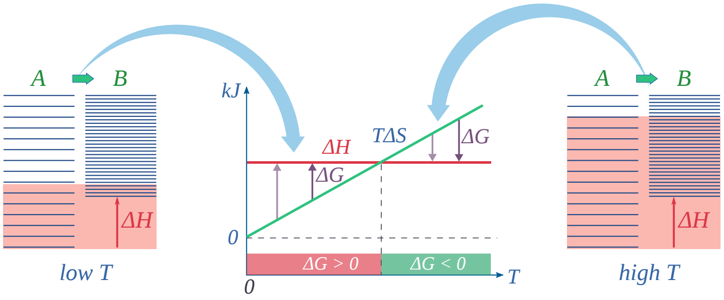


Figure 14.3.3: A hypothetical A $\longrightarrow$ B reaction that is not favored enthalpically and is favored entropically (spontaneous at high temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

Case 4: $\Delta H > 0$ and $\Delta S < 0$

With both ΔH and ΔS working against it, this kind of process will not proceed spontaneously at any temperature. Substance A always has a greater number of accessible energy states, and is therefore always the preferred form.

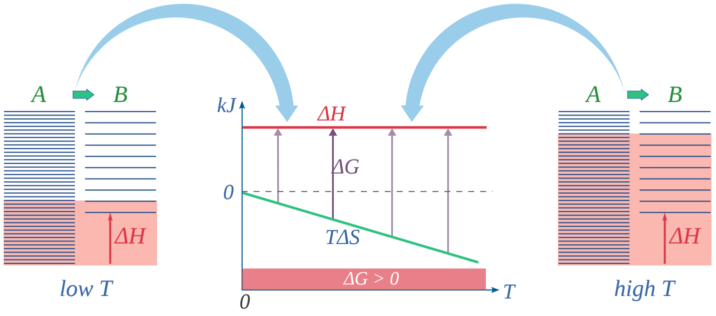


Figure 14.3.4: A hypothetical A $\longrightarrow$ B reaction that is not favored enthalpically and is not is favored entropically (not spontaneous at temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

The plots above are the important ones; do not try to memorize them, but make sure you understand and can explain or reproduce them for a given set of ΔH and ΔS.

- Their most important differentiating features are the position of the ΔH line (above or below the is $T\Delta S$ line), and the slope of the latter, which of course depends on the sign of ΔS.
- The reaction A → B will occur spontaneously only when ΔG is negative (blue arrows pointing down.)
- $T\Delta S$ plots are not quite straight lines as shown here. Similarly, the lines representing ΔH are even more curved.

The other two plots on each diagram are only for the chemistry-committed.

- Each pair of energy-level diagrams depicts the relative spacing of the microscopic energy levels in the reactants and products as reflected by the value of $\Delta S°$. (The greater the entropy, the more closely-spaced are the quantized microstates.)
- The red shading indicates the range of energy levels that are accessible to the system at each temperature. The spontaneous direction of the reaction will always be in the direction in which the red shading overlaps the greater number of energy levels, resulting in the maximum dispersal of thermal energy.
- Note that the vertical offsets correspond to $\Delta H°$ for the reaction.
- Never forget that it is the ability of thermal energy to spread into as many of these states as possible that determines the tendency of the process to take place. None of this is to scale, of course!

The Standard Gibbs Energy

You have already been introduced to the terms such as ΔU^o and ΔH^o in which the ^{o} sign indicates that all components (reactants and products) are in their *standard states*. This concept of standard states is especially important in the case of the free energy, so let's take a few moments to review it. More exact definitions of the conventional standard states can be found in most physical chemistry textbooks. In specialized fields such as biochemistry and oceanography, alternative definitions may apply. For example, the "standard pH" of zero (corresponding to $[H^+] = 1\,M$) is impractical in biochemistry, so pH = 7 is commonly employed. For most practical purposes, the following definitions are good enough:

- **gases:** 1 atmosphere partial pressure
- **pure liquids:** the liquid under a total (hydrostatic) pressure of 1 atm.
- **solutes:** an effective concentration of 1 mol L^{-1} (1 mol dm^{-3}). ("Effective" concentrations approach real concentrations as the latter approach zero; for practical purposes, these can be considered identical at real concentrations smaller than about 10^{-4} molar.)
- **solids:** the pure solid under 1 atm pressure

Reminder on Standard States

- There is actually no "standard temperature", but because most thermodynamics tables list values for 298.15 K (25° C), this temperature is usually implied.
- These same definitions apply to standard enthalpies and internal energies.
- Do not confuse these thermodynamic standard states with the "standard temperature and pressure" (STP) widely employed in gas law calculations.

To make use of Gibbs energies to predict chemical changes, we need to know the free energies of the individual components of the reaction. For this purpose we can combine the standard enthalpy of formation and the standard entropy of a substance to get its **standard free energy of formation**

$$\Delta G_f^o = \Delta H_f^o - T\Delta S_f^o \tag{14.3.8}$$

Recall that the symbol ° refers to the *standard state* of a substance measured under the conditions of 1 atm pressure or an effective concentration of 1 mol L^{-1} and a temperature of 298 K. Then determine the standard Gibbs energy of the reaction according to

$$\Delta G^o = \sum \Delta G_f^o\ (\text{products}) - \sum \Delta G_f^o\ (\text{reactants}) \tag{14.3.9}$$

As with standard heats of formation, the standard free energy of a substance represents the free energy change associated with the formation of the substance from the elements in their most stable forms as they exist under the standard conditions of 1 atm pressure and 298 K. Standard Gibbs free energies of formation are normally found directly from tables. Once the values for all the reactants and products are known, the standard Gibbs energy change for the reaction is found by Equation 14.3.8. Most tables of thermodynamic values list ΔG_f^o values for common substances (e.g., Table T2), which can, of course, always be found from values of $\Delta H_f°$ and $\Delta S_f°$.

✓ Example 14.3.1

Find the standard Gibbs energy change for the reaction

$$\mathrm{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}$$

The $\Delta G_f^{o\,\circ}$ values for the three components of this reaction system are $\mathrm{CaCO_3(s)}$: –1128 kJ $\mathrm{mol^{-1}}$, CaO(*s*): –603.5 kJ $\mathrm{mol^{-1}}$, CO_2(*g*): –137.2 kJ $\mathrm{mol^{-1}}$.

Solution

Substituting into Equation 14.3.8, we have

$$\Delta G^o = (-603.5 – 137.2) – (-1128) kJ\, mol^{-1} = +130.9\, kJ\, mol^{-1}$$

This indicates that the process is not spontaneous under standard conditions (i.e., solid calcium carbone will not form solid calcium oxide and CO_2 at 1 atm partial pressure at 25° C).

Comment: This reaction is carried out on a huge scale to manufacture cement, so it is obvious that the process can be spontaneous under different conditions.

The practical importance of the Gibbs energy is that it allows us to make predictions based on the properties ($\Delta G°$ values) of the reactants and products themselves, eliminating the need to experiment. But bear in mind that while thermodynamics always correctly predicts whether a given process *can* take place (is spontaneous in the thermodynamic sense), it is unable to tell us if it *will* take place at an observable rate.

> *When thermodynamics says "no", it means exactly that. When it says "yes", it means "maybe".*

✓ Example 14.3.2

The reaction

$$\mathrm{\tfrac{1}{2}O_2(g) + H_2(g) \rightarrow H_2O(l)}$$

is used in fuel cells to produce an electrical current. The reaction can also be carried out by direct combustion.

Thermodynamic data: molar entropies in J $\mathrm{mol^{-1}\,K^{-1}}$: O_2(g) 205.0; H_2(g)130.6; H_2O(l) 70.0; H_2O(l) $\Delta H°_f$ = –285.9 kJ $\mathrm{mol^{-1}}$.

Use this information to find

a. The amount of heat released when the reaction takes place by direct combustion;
b. The amount of electrical work the same reaction can perform when carried out in a fuel cell at 298 K under reversible conditions;
c. The amount of heat released under the same conditions.

Solution

First, we need to find ΔH^o and ΔS^o for the process. Recalling that the standard enthalpy of formation of the elements is zero,

$$\begin{aligned} \Delta H^o &= \Delta H_f^p(\text{products}) – \Delta H_f^\circ(\text{reactants}) \\ &= –285.9\, kJ\, mol^{-1} – 0 \\ &= –285.9\, kJ\, mol^{-1} \end{aligned}$$

Similarly,

$$\begin{aligned} \Delta S^o &= S_f^o(\text{products}) – S_f^o(\text{reactants}) \\ &= (70.0) – (½ \times 205.0 + 130.6) \\ &= –163\, J\, K^{-1} mol^{-1} \end{aligned}$$

a. When the hydrogen and oxygen are combined directly, the heat released will be $\Delta H^o = –285.9\, kJ\, mol^{-1}$.

b. The maximum electrical work the fuel cell can perform is given by

$$\begin{aligned} \Delta G^o &= \Delta H^o - T\Delta S^o \\ &= -285.9\, kJ\, mol^{-1} - (298\, K)(-163\, J K^{-1} mol^{-1}). \\ &= -237.2\, kJ\, mol^{-1}. \end{aligned}$$

c. The heat released in the fuel cell reaction is the difference between the enthalpy change (the total energy available) and the reversible work that was expended:

$$\begin{aligned} \Delta H^o - \Delta G^o &= T\Delta S^o \\ &= (298\, K)(-163\, J K^{-1} mol^{-1}) \\ &= -48,800\, J\, mol^{-1} \\ &= -48.8\, kJ\, mol^{-1}. \end{aligned}$$

The foregoing example illustrates an important advantage of fuel cells. Although direct combustion of a mole of hydrogen gas yields more energy than is produced by the same net reaction within the fuel cell, the latter, in the form of electrical energy, can be utilized at nearly 100-percent energy efficiency by a motor or some other electrical device. If the thermal energy released by direct combustion were supplied to a heat engine, second-law considerations would require that at least half of this energy be "wasted" to the surroundings.

ΔG vs. $\Delta G°$: what's the difference?

$\Delta G°$ refer to *single, specific chemical changes* in which all components (reactants and products) are in their *standard states*.

The ΔG_f^o of a substance, like ΔH_f^o, refers to the reaction in which that substance is formed from the elements as they exist in their most stable forms at 1 atm pressure and (usually) 298 K. Both of these terms are by definition zero for the elements in their standard states. There are only a few common cases in which this might create some ambiguity:

Table 14.3.1: Standard Gibbs Energies of Select Substances

Stable Form	ΔG_f^o (kJ mol^{-1})	Unstable Form	ΔG_f^o (kJ mol^{-1})
$O_2(g)$	0	$O_3(g)$	163.2
$C(graphite)$	0	$C(diamond)$	2.9
$S(rhombic)$	0	$S(monoclinic)$	0.1
$P(white)$	0	$P_4(g)$	24.4

Ions in aqueous solution are a special case; their standard free energies are relative to the hydrated hydrogen ion $H^+(aq)$ which is assigned $\Delta G_f^o = 0$.

ΔG is very different from ΔG°. The distinction is nicely illustrated in Figure $14.3.5$ in which ΔG is plotted on a vertical axis for two hypothetical reactions having opposite signs of ΔG°. The horizontal axis schematically expresses the relative concentrations of reactants and products at any point of the process. Note that the origin corresponds to the composition at which half of the reactants have been converted into products.

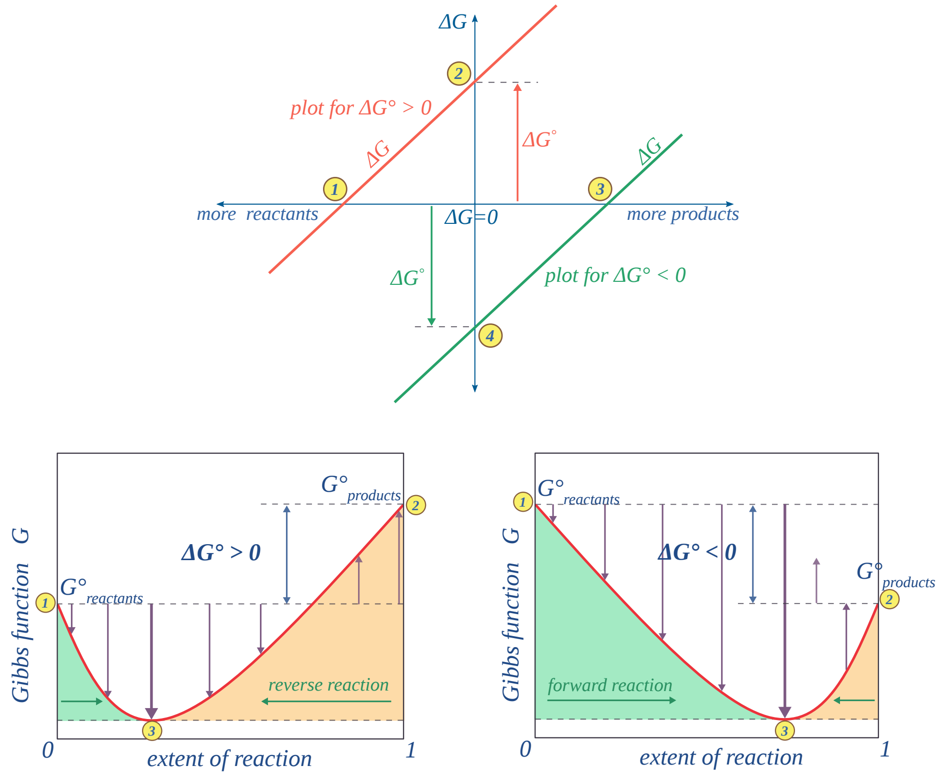


Figure 14.3.5: (CC BY 4.0; Ümit Kaya via LibreTexts)

Take careful note of the following:

- for the $\Delta G^\circ > 0$ reaction. Notice that there are an infinite number of these values, depending on the progress of the reaction. In contrast there is only a single value ② of ΔG°, corresponding to the composition at which $\Delta G = 0$ (①).
- At this point, some products have been formed, but the composition is still dominated by reactants.
- If we begin at a composition to the left of ①, ΔG will be negative and the composition will move to the right. Similarly if we begin with a composition to the right of ①, ΔG will be positive and the composition will move to the left.
- The plot on the right is for the $\Delta G^\circ < 0$ reaction, for which ΔG° is shown at ④. At its equilibrium point ③, there are more products than reactants. If we start at a composition to the right of ③, the composition will tend to move to the left. If the initial composition is to the left of ③, the reaction will tend to proceed to the right.
- What would happen if ΔG° were 0? The equilibrium point of such a reaction would be at the origin, corresponding to half the reactants being converted to products.

The important principle you should understand from this is that a negative ΔG° does not mean that the reactants will be completely transformed into products. By the same token, a positive ΔG° does not mean that no products are formed at all.

It should now be clear from the discussion above that a given reaction carried out under standard conditions is characterized by a *single value* of ΔG°.

The reason for the Gibbs energy minimum at equilibrium relates to the increase in entropy when products and reactants coexist in the same phase. As seen in the plot, even a minute amount of "contamination" of products by reactants reduces the free energy below that of the pure products. In contrast, composition of a chemical reaction system undergoes continual change until the equilibrium state is reached. So the a single reaction can have an infinite number of ΔG values, reflecting the infinite possible compositions between the extremes of pure reactants (zero extent of reaction) and pure products (unity extent of reaction).

In the example of a reaction A → B, depicted in the above diagram, the standard free energy of the products ② is smaller than that of the reactants ①, so the reaction will take place spontaneously. This does not mean that each mole of pure A will be converted into one mole of pure B. For reactions in which products and reactants occupy a single phase (gas or solution), the meaning of "spontaneous" is that the equilibrium composition ③ will correspond to an extent of reaction greater than 0.5 but smaller than unity.Note, however, that for ΔG° values in excess of about ± 50 kJ mol^{-1}, the equilibrium composition will be negligibly different from zero or unity extent-of-reaction. The physical meaning of ΔG is that it tells us how far the free energy of the system has changed from $G°$ of the pure reactants ①. As the reaction proceeds to the right, the composition changes, and ΔG begins to fall. When the composition reaches ③, ΔG reaches its minimum value and further reaction would cause it to rise. But because free energy can only decrease but never increase, this does not happen. The composition of the system remains permanently at its equilibrium value.

A G *vs*. extent-of-reaction diagram for a non-spontaneous reaction can be interpreted in a similar way; the equilibrium composition ③ will correspond to an extent of reaction greater than zero but less than 0.5. In this case, the minimum at ③ reflects the increase in entropy when the reactants are "contaminated" by a small quantity of products.

If all this detail about ΔG seems a bit overwhelming, do not worry: it all gets hidden in the equilibrium constant and reaction quotient that we discuss in the next lesson!

Interpretation of Standard Gibbs energy changes

Although it is ΔG rather than ΔG^o that serves as a criterion for spontaneous change at constant temperature and pressure, ΔG^o values are so readily available that they are often used to get a rough idea of whether a given chemical change is possible. This is practical to do in some cases, but not in others:

✓ Example

It generally works for reactions such as

$$4\,\mathrm{NH_3(g)} + 5\,\mathrm{O_2(g)} \rightarrow 4\,\mathrm{NO(g)} + 6\,\mathrm{H_2O(g)}$$

with $\Delta G^o = -1,010\ kJ$.

(industrially important for the manufacture of nitric acid) because ΔG^o is so negative that the reaction will be spontaneous and virtually complete under just about any reasonable set of conditions.

✓ Example

The following reaction expresses the fact that the water molecule is thermodynamically stable:

$$2\,\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{H_2O(l)}$$

with $\Delta G^o = -237.2\ kJ$.

Note that this refers to *liquid* water (the standard state of H_2O at 25°). If you think about it, a negative standard Gibbs energy of formation (of which this is an example) can in fact be considered a definition of molecular stability.

✓ Example

Similarly, dissociation of dihydrogen into its atoms is highly unlikely under standard conditions:

$$\mathrm{H_2O(g)} \rightarrow 2\,\mathrm{H(g)} + \mathrm{O(g)}$$

with $\Delta G^o = +406.6\ kJ$.

Again, an analogous situation would apply to any stable molecule.

✓ Example

Now consider the dissociation of dinitrogen tetroxide

$$\mathrm{N_2O_4(g)} \rightarrow 2\,\mathrm{NO_2(g)}$$

with $\Delta G^o = +2.8 kJ$.

in which the positive value of $\Delta G°$ tells us that N_2O_4 at 1 atm pressure will not change into two moles of NO_2 at the same pressure, but owing to the small absolute value of $\Delta G°$, we can expect the spontaneity of the process to be quite sensitive to both the temperature (as shown in the table below) and to the pressure in exactly the way the Le Chatelier principle predicts.

Example

For reactions involving dissolved ions, one has to be quite careful. Thus for the dissociation of the weak hydrofluoric acid

$$\mathrm{HF(aq)} \rightarrow \mathrm{H^+(aq)} + \mathrm{F-(aq)}$$

with $\Delta G^o = -317\, kJ$.

it is clear that a 1 mol/L solution of HF will not dissociate into 1M ions, but this fact is not very useful because if the HF is added to water, the initial concentration of the fluoride ion will be zero (and that of H^+ very close to zero), and the Le Chatelier principle again predicts that *some* dissociation will be spontaneous.

Example

It is common knowledge that dissociation of water into hydrogen- and hydroxyl ions occurs only very sparingly:

$$\mathrm{H_2O(l)} \rightarrow \mathrm{H^+(aq)} + \mathrm{OH-(aq)}$$

with $\Delta G^o = 79.9\, kJ$.

which correctly predicts that the water will not form 1M (effective concentration) of the ions, but this is hardly news if you already know that the product of these ion concentrations can never exceed 10^{-14} at 298K.

Example

Finally, consider this most familiar of all phase change processes, the vaporization of liquid water:

$$\mathrm{H_2O(l)} \rightarrow \mathrm{H_2O(g)}$$

with $\Delta G^o = 8.58\, kJ$.

Conversion of liquid water to its vapor at 1 atm partial pressure does not take place at 25° C, at which temperature the equilibrium partial pressure of the vapor (the "vapor pressure") is only 0.031 atm (23.8 torr.) Gaseous H_2O at a pressure of 1 atm can only exist at 100° C. Of course, water left in an open container at room temperature will spontaneously evaporate if the partial pressure of water vapor in the air is less than 0.031 atm, corresponding to a relative humidity of under 100%

Finding the Equilibrium Temperature

A reaction is in its equilibrium state when

$$\Delta G = \Delta H - T\Delta S = 0 \tag{14.3.10}$$

The temperature at which this occurs is given by

$$T = \frac{\Delta H}{\Delta S} \tag{14.3.11}$$

If we approximate ΔH by ΔH^o and ΔS by ΔS^o, so Equation 14.3.10would be

$$\Delta G \approx \Delta H^o - T\Delta S^o = 0 \tag{14.3.12}$$

We can then estimate the normal boiling point of a liquid. From the following thermodynamic data for water:

$H_2O(l)$	→	$H_2O(g)$	
−285.9		−241.8	ΔH° = +44.1 kJ
69.9		188.7	ΔS° = +118.7 J K^{-1}

Caution!

Because ΔH° values are normally expressed in kilojoules while ΔS° is given in joules, a very common student error is to overlook the need to express both in the same units.

We find that liquid water is in equilibrium with water vapor at a partial pressure of 1 atm when the temperature is

$$T = \frac{44,100\,J}{118.7\,J\,K^{-1}} = 371.5\,K \tag{14.3.13}$$

But "*the normal boiling point of water is 373 K*", you say? Very true. The reason we are off here is that both $\Delta H°$ and $\Delta S°$ have their own temperature dependencies; we are using the "standard" 25° values without correcting them to 100° C. Nevertheless, if you think about it, the fact that we can estimate the boiling point of a liquid from a table of thermodynamic data should be rather impressive! Of course, the farther one gets from 298 K, the more unreliable will be the result. Thus for the dissociation of dihydrogen into its atoms,

$H_2(g)$	→	$2\ H(g)$	
0		2 x (218.0)	$\Delta H° = +436.0$ kJ
130.6		2 x (114.6)	$\Delta S° = +98.6\ J\ K^{-1}$

$$T = \frac{436,000\,J}{98.6\,J\,K^{-1}} = 4,420\,K \tag{14.3.14}$$

All one can say here is that H_2 will break down at something over 3000 K or so. (You may already know that *all* molecules will dissociate into their atoms at high temperatures.) We tend to think of high temperatures as somehow "forcing" molecules to dissociate into their atoms, but this is wrong. In order to get the H–H bond to vibrate so violently through purely thermal excitation that the atoms would fly apart, a temperature more like 30,000 K would be required. The proper interpretation is at the temperature corresponding to *ΔH/TΔS*, the molecule *spontaneously* absorbs energy from the surroundings sufficient to overcome the H-H bond strength.

Predicting the Effects of Temperature

The $T\Delta S$ term interacts with the ΔH term in ΔG to determine whether the reaction can take place at a given temperature. This can be more clearly understood by examining plots of $T\Delta S^o$ and ΔH^o as functions of the temperature for some actual reactions. Of course these parameters refer to standard states that generally do not correspond to the temperatures, pressures, or concentrations that might be of interest in an actual case. Nevertheless, these quantities are easily found and they can usefully predict the way that temperature affects these systems.

Case 1: Exothermic reaction, ΔS° > 0

$$\mathrm{C(graphite) + O_2(g) \rightarrow CO_2(g)}$$

- $\Delta H^o = –393\,kJ$
- $\Delta G^o = –394\,kJ$ at $298\,K$

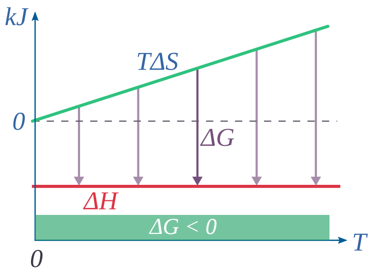


Figure 14.3.6: (CC BY 4.0; Ümit Kaya via LibreTexts)

This *combustion reaction*, like most such reactions, is **spontaneous at all temperatures**. The positive entropy change is due mainly to the greater mass of CO_2 molecules compared to those of O_2.

Case 2: Exothermic reaction, $\Delta S° < 0$

$$3\,H_2 + N_2 \rightarrow 2\,NH_3(g)$$

- $\Delta H^o = -46.2\,kJ$
- $\Delta G^o = -16.4\,kJ$ at $298\,K$

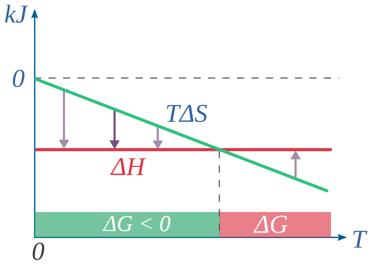


Figure 14.3.7: (CC BY 4.0; Ümit Kaya via LibreTexts)

The decrease in moles of gas in the **Haber ammonia synthesis** drives the entropy change negative, making the reaction **spontaneous only at low temperatures**. Thus higher T, which speeds up the reaction, also reduces its extent.

Case 3: Endothermic reaction, $\Delta S° > 0$

$$N_2O_4(g) \rightarrow 2\,NO_2(g)$$

- $\Delta H^o = 55.3\,kJ$
- $\Delta G^o = +2.8\,kJ$ at $298\,K$

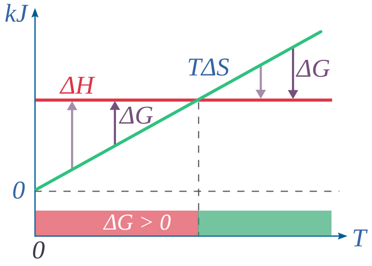


Figure 14.3.8: (CC BY 4.0; Ümit Kaya via LibreTexts)

Dissociation reactions are typically endothermic with positive entropy change, and are therefore **spontaneous at high temperatures**. Ultimately, all molecules decompose to their atoms at sufficiently high temperatures.

Case 4: Endothermic Reaction, $\Delta S° < 0$

$$\tfrac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$$

- $\Delta H^\circ = 33.2\,kJ$
- $\Delta S^o = -249\,J\,K^{-1}$
- $\Delta G^o = +51.3\,kJ$ at $298\,K$

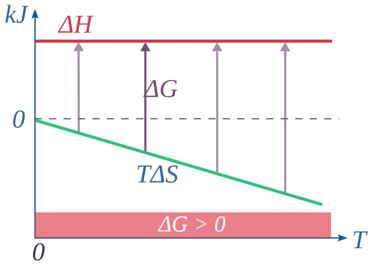


Figure 14.3.9: (CC BY 4.0; Ümit Kaya via LibreTexts)

This reaction is **not spontaneous at any temperature**, meaning that *its reverse is always spontaneous*. But because the reverse reaction is kinetically inhibited, NO_2 can exist indefinitely at ordinary temperatures even though it is thermodynamically unstable.

Concluding remarks on Gibbs Energy

The appellation “free energy” for G has led to so much confusion that many scientists now refer to it simply as the *Gibbs energy*. The “free” part of the older name reflects the steam-engine origins of thermodynamics with its interest in converting heat into work: ΔG is the maximum amount of energy, which can be “freed” from the system to perform useful work. By "useful", we mean work other than that which is associated with the expansion of the system. This is most commonly in the form of electrical work (moving electric charge through a potential difference), but other forms of work (osmotic work, increase in surface area) are also possible.

A much more serious difficulty with the Gibbs function, particularly in the context of chemistry, is that although G has the *units* of energy (joules, or in its intensive form, J mol^{-1}), it lacks one of the most important attributes of energy in that it is not *conserved*. Thus, although the free energy always falls when a gas expands or a chemical reaction takes place spontaneously, there need be no compensating *increase* in energy anywhere else. Referring to G as an energy also reinforces the false but widespread notion that a fall in energy must accompany any change. But if we accept that energy is conserved, it is apparent that the only necessary condition for change (whether the dropping of a weight, expansion of a gas, or a chemical reaction) is the *redistribution* of energy. The quantity \(–Δ*G*\) associated with a process represents the quantity of energy that is “shared and spread”, which as we have already explained is the meaning of the increase in the entropy. The quotient $-\Delta G/T$ is in fact identical with ΔS_{total}, the entropy change of the world, whose increase is the primary criterion for any kind of change.

G differs from the thermodynamic quantities H and S in another significant way: it has no physical reality as a property of matter, whereas H and S can be related to the quantity and distribution of energy in a collection of molecules. The free energy is simply a useful construct that serves as a criterion for change and makes calculations easier.

What Gibbs Energy is not...

- Gibbs Energy is not free energy
- Gibbs Energy is not energy
- Gibbs Energy is not even "real"

14.4: The Law of Mass Action for Related and Simultaneous Equilibria

Learning Objectives

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.

Relationship among Equilibrium Expressions

Chemists frequently need to know the equilibrium constant for a reaction that has not been previously studied. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated values for the other reactions.

To illustrate this procedure, let's consider the reaction of N_2 with O_2 to give NO_2. This reaction is an important source of the NO_2 that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps. In the first reaction (1), N_2 reacts with O_2 at the high temperatures inside an internal combustion engine to give NO. The released NO then reacts with additional O_2 to give NO_2 (2). The equilibrium constant for each reaction at 100°C is also given.

1. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \qquad K_1 = 2.0 \times 10^{-25}$
2. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_2 = 6.4 \times 10^{9}$

Summing reactions (1) and (2) gives the overall reaction of N_2 with O_2:

3. $N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_3 = ?$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2} \tag{14.4.1}$$

What is the relationship between K_1, K_2, and K_3, all at 100°C? The expression for K_1 has $[NO]^2$ in the numerator, the expression for K_2 has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for K_3. Multiplying K_1 by K_2 and canceling the $[NO]^2$ terms,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3 \tag{14.4.2}$$

Thus the product of the equilibrium constant expressions for K_1 and K_2 is the same as the equilibrium constant expression for K_3:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^{9}) = 1.3 \times 10^{-15} \tag{14.4.3}$$

The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions. In contrast, recall that according to Hess's Law, ΔH for the sum of two or more reactions is the sum of the ΔH values for the individual reactions.

Note

To determine K for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.

Example 14.4.6

The following reactions occur at 1200°C:

1. $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \qquad K_1 = 9.17 \times 10^{-2}$
2. $CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)} \qquad K_2 = 3.3 \times 10^{4}$

Calculate the equilibrium constant for the following reaction at the same temperature.

3. $CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \qquad K_3 = ?$

Given: two balanced equilibrium equations, values of K, and an equilibrium equation for the overall reaction

Asked for: equilibrium constant for the overall reaction

Strategy:

Arrange the equations so that their sum produces the overall equation. If an equation had to be reversed, invert the value of K for that equation. Calculate K for the overall equation by multiplying the equilibrium constants for the individual equations.

Solution:

The key to solving this problem is to recognize that reaction 3 is the sum of reactions 1 and 2:

$$CO_{(g)} + 3\cancel{H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)} \tag{14.4.4}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 3\cancel{H_{2(g)}} + H_{2(g)} \tag{14.4.5}$$

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \tag{14.4.6}$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^4) = 3.03 \times 10^3 \tag{14.4.7}$$

? Exercise 14.4.6

In the first of two steps in the industrial synthesis of sulfuric acid, elemental sulfur reacts with oxygen to produce sulfur dioxide. In the second step, sulfur dioxide reacts with additional oxygen to form sulfur trioxide. The reaction for each step is shown, as is the value of the corresponding equilibrium constant at 25°C. Calculate the equilibrium constant for the overall reaction at this same temperature.

1. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)} \qquad K_1 = 4.4 \times 10^{53}$
2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_2 = 2.6 \times 10^{12}$
3. $\frac{1}{8}S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_3 = ?$

Answer

$K_3 = 1.1 \times 10^{66}$

Summary

An equilibrium system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium. When a reaction can be expressed as the sum of two or more reactions, its equilibrium constant is equal to the product of the equilibrium constants for the individual reactions.

14.5: Equilibrium Calculations for Gas-Phase and Heterogenous Reactions

Learning Objectives

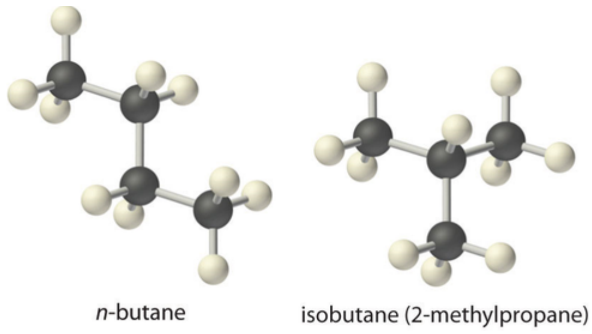
- To solve quantitative problems involving chemical equilibriums.

There are two fundamental kinds of equilibrium problems:

1. those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and
2. those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

Calculating an Equilibrium Constant from Equilibrium Concentrations

The equilibrium constant for the decomposition of $CaCO_{3(s)}$ to $CaO_{(s)}$ and $CO_{2(g)}$ is $K = [CO_2]$. At 800°C, the concentration of CO_2 in equilibrium with solid $CaCO_3$ and CaO is $2.5 \times 10^{-3}\ M$. Thus K at 800°C is 2.5×10^{-3} (remember that equilibrium constants are unitless). A more complex example of this type of problem is the conversion of n-butane, an additive used to increase the volatility of gasoline, into isobutane (2-methylpropane).



This reaction can be written as follows:

$$\text{n}-\text{butane}_{(\text{g})} \rightleftharpoons \text{isobutane}_{(\text{g})} \tag{14.5.1}$$

and the equilibrium constant $K = [\text{isobutane}]/[\text{n-butane}]$. At equilibrium, a mixture of n-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M n-butane. Substituting these concentrations into the equilibrium constant expression,

$$\begin{aligned} K &= \frac{[\text{isobutane}]}{[\backslash\text{texT}n - butane]} \\ &= \frac{0.041\ M}{0.016\,M} \\ &= 2.6 \end{aligned}$$

Thus the equilibrium constant for the reaction as written is 2.6.

Example 14.5.1

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:

$$2\,\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\,\text{SO}_3(\text{g})$$

A mixture of SO_2 and O_2 was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained

- $5.0 \times 10^{-2}\ M\ SO_3$,

- $3.5 \times 10^{-3}\ M\ O_2$, and
- $3.0 \times 10^{-3}\ M\ SO_2$.

Calculate K and K_p at this temperature.

Given: balanced equilibrium equation and composition of equilibrium mixture

Asked for: equilibrium constant

Strategy

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain K.

Solution

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(5.0 \times 10^{-2})^2}{(3.0 \times 10^{-3})^2(3.5 \times 10^{-3})} = 7.9 \times 10^4$$

To solve for K_p, we need to identify Δn where $\Delta n = 2 - 3 = -1$ and then

$$K_p = K(RT)^{\Delta n}$$

$$K_p = 7.9 \times 10^4 [(0.08206\ L \cdot atm/mol \cdot K)(800 K)]^{-1}$$

$$K_p = 1.2 \times 10^3$$

? Exercise 14.5.1

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)}$$

A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained

- $1.37 \times 10^{-2}\ M\ HI$,
- $6.47 \times 10^{-3}\ M\ H_2$, and
- $5.94 \times 10^{-4}\ M\ I_2$.

Calculate K and K_p for this reaction.

Answer (K)

$K = 48.8$

Answer (K_p)

$K_p = 48.8$

Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example $14.5.2$ shows one way to do this.

✓ Example 14.5.2

A 1.00 mol sample of $NOCl$ was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl_2. Calculate K at this temperature. The equation for the decomposition of $NOCl$ to NO and Cl_2 is as follows:

$$\mathrm{2\,NOCl(g) \rightleftharpoons 2\,NO(g) + Cl_2(g)}$$

Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium

Asked for: K

Strategy:

A. Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).
B. Calculate all possible initial concentrations from the data given and insert them in the table.
C. Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.
D. Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

Solution

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K=\frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of $NOCl$, NO, and Cl_2 at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)}+Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial			
Change			
Final			

B Initially, the system contains 1.00 mol of $NOCl$ in a 2.00 L container. Thus $[NOCl]_i=1.00\ mol/2.00\ L=0.500\ M$ The initial concentrations of NO and Cl_2 are $0\ M$ because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f=0.056\ mol/2.00\ L=0.028\ M$ We insert these values into the following table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)}+Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change			
Final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

$$\Delta[Cl_2]=0.028\ M_{(final)}-0.00\ M_{(initial)}]=+0.028\ M$$

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta[NO]=\left(\frac{0.028\ \ mol\ \cancel{Cl_2}}{L}\right)\left(\frac{2\ mol\ NO}{1\ \ mol\ \cancel{Cl_2}}\right)=0.056\ M$$

Similarly, 2 mol of $NOCl$ are consumed for every 1 mol of Cl_2 produced, so the change in the $NOCl$ concentration is as follows:

$$\Delta[NOCl] = \left(\frac{0.028\ \ mol\ \cancel{Cl_2}}{L}\right)\left(\frac{-2\ mol\ NOCl}{1\ \ mol\ \cancel{Cl_2}}\right) = -0.056\ M$$

We insert these values into our table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change	−0.056	+0.056	+0.028
Final			0.028

D We sum the numbers in the $[NOCl]$ and $[NO]$ columns to obtain the final concentrations of NO and $NOCl$:

$$[NO]_f = 0.000\ M + 0.056\ M = 0.056\ M$$

$$[NOCl]_f = 0.500\ M + (-0.056\ M) = 0.444 M$$

We can now complete the table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2(0.028)}{(0.444)^2} = 4.5 \times 10^{-4}$$

Exercise 14.5.2

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting $0.1248\ M\ H_2$ and $0.0416\ M\ N_2$ at about 500°C. At equilibrium, the mixture contained 0.00272 M NH_3. What is K for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

at this temperature? What is K_p?

Answer (K)

$$K = 0.105$$

Answer (K_p)

$$K_p = 2.61 \times 10^{-5}$$

Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of n-butane to isobutane (Equation 14.5.1), for which K = 2.6 at 25°C. If we begin with a 1.00 M sample of n-butane, we can determine the concentration of n-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example 14.5.2

$$\text{n-butane}(g) \rightleftharpoons \text{isobutane}(g) \tag{14.5.2}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial		
Change		
Final		

The initial concentrations of the reactant and product are both known: [n-butane]i = 1.00 M and [isobutane]i = 0 M. We need to calculate the equilibrium concentrations of both n-butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the change in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as +x, then the change in the concentration of n-butane is Δ[n-butane] = −x. This is because the balanced chemical equation for the reaction tells us that 1 mol of n-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{14.5.3}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial	1.00	0
Change	−x	+x
Final	(1.00 − x)	(0 + x) = x

Substituting the expressions for the final concentrations of n-butane and isobutane from the table into the equilibrium equation,

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \frac{x}{1.00 - x} = 2.6 \tag{14.5.4}$$

Rearranging and solving for x,

$$\begin{aligned} x &= 2.6(1.00 - x) = 2.6 - 2.6x \\ x + 2.6x &= 2.6 \\ x &= 0.72 \end{aligned}$$

We obtain the final concentrations by substituting this x value into the expressions for the final concentrations of n-butane and isobutane listed in the table:

$$[\text{n-butane}]_f = (1.00 - x)M = (1.00 - 0.72)M = 0.28\ M \tag{14.5.5}$$

$$[\text{isobutane}]_f = (0.00 + x)M = (0.00 + 0.72)M = 0.72\ M \tag{14.5.6}$$

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same K that we used in the calculation:

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \left(\frac{0.72\ \cancel{M}}{0.28\ \cancel{M}}\right) = 2.6 \tag{14.5.7}$$

This is the same K we were given, so we can be confident of our results.

Example $14.5.3$ illustrates a common type of equilibrium problem that you are likely to encounter.

Example $14.5.3$

The water–gas shift reaction is important in several chemical processes, such as the production of H_2 for fuel cells. Thisreaction can be written as follows:

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

$K = 0.106$ at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?

Given: balanced equilibrium equation, K, and initial concentrations

Asked for: final concentrations

Strategy:

A. Construct a table showing what is known and what needs to be calculated. Define x as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of x. From the values in the table, calculate the final concentrations.
B. Write the equilibrium equation for the reaction. Substitute appropriate values from the ICE table to obtain x.
C. Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150\ M$. Just as before, we will focus on the change in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as x, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of x. For example, 1 mol of CO is produced for every 1 mol of H_2O, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
Initial	0.0150	0.0150	0	0
Change	−x	−x	+x	+x
Final	(0.0150 − x)	(0.0150 − x)	x	x

B We can now use the equilibrium equation and the given K to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(x)(x)}{(0.0150-x)(0.0150-x)} = \frac{x^2}{(0.0150-x)^2} = 0.106$$

We could solve this equation with the quadratic formula, but it is far easier to solve for x by recognizing that the left side of the equation is a perfect square; that is,

$$\frac{x^2}{(0.0150-x)^2} = \left(\frac{x}{0.0150-x}\right)^2 = 0.106$$

Taking the square root of the middle and right terms,

$$\frac{x^2}{(0.0150-x)^2} = (0.106)^{1/2} = 0.326$$

$$x = (0.326)(0.0150) - 0.326x$$

$$1.326x = 0.00489$$

$$x = 0.00369 = 3.69 \times 10^{-3}$$

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f = [H_2]_i + \Delta[H_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = (0 + 0.00369)\ M = 0.00369\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = (0 + 0.00369)\ M = 0.00369\ M$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

? Exercise 14.5.3

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$K = 54$ at 425°C. If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer

$[HI]_f = 0.270\ M\ [H_2]_f = [I_2]_f = 0.037\ M$

In Example $14.5.3$, the initial concentrations of the reactants were the same, which gave us an equation that was a perfect square and simplified our calculations. Often, however, the initial concentrations of the reactants are not the same, and/or one or more of the products may be present when the reaction starts. Under these conditions, there is usually no way to simplify the problem, and we must determine the equilibrium concentrations with other means. Such a case is described in Example $14.5.4$.

✓ Example 14.5.4

In the water–gas shift reaction shown in Example $14.5.3$, a sample containing 0.632 M $\mathrm{CO_2}$ and 0.570 M $\mathrm{H_2}$ is allowed to equilibrate at 700 K. At this temperature, $K = 0.106$. What is the composition of the reaction mixture at equilibrium?

Given: balanced equilibrium equation, concentrations of reactants, and K

Asked for: composition of reaction mixture at equilibrium

Strategy:

A. Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations (x) and the final concentrations.
B. Write the equilibrium constant expression for the reaction. Substitute the known K value and the final concentrations to solve for x.
C. Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A $[CO_2]_i = 0.632\ M$ and $[H_2]_i = 0.570\ M$. Again, x is defined as the change in the concentration of H_2O: $\Delta[H_2O] = +x$. Because 1 mol of CO is produced for every 1 mol of H_2O, the change in the concentration of CO is the same as the change in the concentration of H2O, so Δ[CO] = +x. Similarly, because 1 mol each of H_2 and CO_2 are consumed for every 1 mol of H_2O produced, $\Delta[H_2] = \Delta[CO_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$H_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$	$CO_{(g)}$
Initial	0.570	0.632	0	0
Change	−x	−x	+x	+x
Final	(0.570 − x)	(0.632 − x)	x	x

B We can now use the equilibrium equation and the known K value to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106$$

In contrast to Example 14.5.3, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.20x + x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0$$

This equation can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)}$$

$$x = 0.148 \text{ and } -0.290$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O] = \Delta[CO] = +0.148M$, and $\Delta[H_2] = \Delta[CO_2] = -0.148\ M$.

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f[= [H_2]_i + \Delta[H_2] = 0.570\ M - 0.148\ M = 0.422M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = 0.632\ M - 0.148\ M = 0.484M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = 0\ M + 0.148\ M = 0.148\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = 0M + 0.148\ M = 0.148M$

We can check our work by substituting these values into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.148)^2}{(0.422)(0.484)} = 0.107$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

? Exercise 14.5.4

The exercise in Example 14.5.1 showed the reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K = 54$ at 425°C. If a sample containing 0.200 M H_2 and 0.0450 M I_2 is allowed to equilibrate at 425°C, what is the final concentration of each substance in the reaction mixture?

Answer

$[H_I]_f = 0.0882\ M$

$[H_2]_f = 0.156\ M$

$[I_2]_f = 9.2 \times 10^{-4} M$

In many situations it is not necessary to solve a quadratic (or higher-order) equation. Most of these cases involve reactions for which the equilibrium constant is either very small ($K \leq 10^{-3}$) or very large ($K \geq 10^{3}$), which means that the change in the concentration (defined as x) is essentially negligible compared with the initial concentration of a substance. Knowing this simplifies the calculations dramatically, as illustrated in Example 14.5.5.

✓ Example 14.5.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$\mathrm{N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)} \tag{14.5.8}$$

with $K_p = 2.0 \times 10^{-31}$ at 25°C.

What is the partial pressure of NO in equilibrium with N_2 and O_2 in the atmosphere (at 1 atm) $P_{N_2} = 0.78\ atm$ and $P_{O_2} = 0.21\ atm$?

Given: balanced equilibrium equation and values of K_p, P_{O_2}, and P_{N_2}

Asked for: partial pressure of NO

Strategy:

A. Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.
B. Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration (x).
C. Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for K.

Solution

A Because we are given Kp and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of O_2 is 0.21 atm and that of N_2 is 0.78 atm. If we define the change in the partial pressure of NO as 2x, then the change in the partial pressure of O_2 and of N_2 is −x because 1 mol each of N_2 and of O_2 is consumed for every 2 mol of NO produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

$$\mathrm{N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)} \tag{14.5.9}$$

ICE	P_{N_2}	P_{O_2}	P_{NO}
Initial	0.78	0.21	0
Change	−x	−x	+2x
Final	(0.78 − x)	(0.21 − x)	2x

B Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78-x)(0.21-x)} = 2.0 \times 10^{-31}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very small; therefore, the x value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, (0.78 − x) = 0.78 and (0.21 − x) = 0.21. Substituting these expressions into our original equation,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4}$$

$$x^= 9.1 \times 10^{-17}$$

C Substituting this value of x into our expressions for the final partial pressures of the substances,

- $P_{NO} = 2x\ atm = 1.8 \times 10^{-16}\ atm$
- $P_{N_2} = (0.78 - x)\ atm = 0.78\ atm$
- $P_{O_2} = (0.21 - x)\ atm = 0.21\ atm$

From these calculations, we see that our initial assumption regarding x was correct: given two significant figures, 2.0×10^{-16} is certainly negligible compared with 0.78 and 0.21. When can we make such an assumption? As a general rule, if x is less than about 5% of the total, or $10^{-3} > K > 10^3$, then the assumption is justified. Otherwise, we must use the quadratic formula or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of N_2 and O_2 to a substantial degree at 25°C. We can verify our results by substituting them into the original equilibrium equation:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

The final K_p agrees with the value given at the beginning of this example.

? Exercise 14.5.5

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$3O_{2(g)} \rightleftharpoons 2O_{3(g)}$$

with $K_p = 2.5 \times 10^{-59}$ at 25°C. What ozone partial pressure is in equilibrium with oxygen in the atmosphere ($P_{O_2} = 0.21\ atm$)?

Answer

$4.8 \times 10^{-31}\ atm$

Another type of problem that can be simplified by assuming that changes in concentration are negligible is one in which the equilibrium constant is very large (K ≥ 10^3). A large equilibrium constant implies that the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion. When we solve this type of problem, we view the system as equilibrating from the products side of the reaction rather than the reactants side. This approach is illustrated in Example $14.5.6$.

✓ Example 14.5.6

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

with $K = 9.6 \times 10^{18}$ at 25°C. If a mixture of 0.200 M H_2 and 0.155 M C_2H_4 is maintained at 25°C in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

Given: balanced chemical equation, K, and initial concentrations of reactants

Asked for: equilibrium concentrations

Strategy:

A. Construct a table showing initial concentrations, concentrations that would be present if the reaction were to go to completion, changes in concentrations, and final concentrations.
B. Write the equilibrium constant expression for the reaction. Then substitute values from the table into the expression to solve for x (the change in concentration).

C. Calculate the equilibrium concentrations. Check your answers by substituting these values into the equilibrium equation.

Solution:

A From the magnitude of the equilibrium constant, we see that the reaction goes essentially to completion. Because the initial concentration of ethylene (0.155 M) is less than the concentration of hydrogen (0.200 M), ethylene is the limiting reactant; that is, no more than 0.155 M ethane can be formed from 0.155 M ethylene. If the reaction were to go to completion, the concentration of ethane would be 0.155 M and the concentration of ethylene would be 0 M. Because the concentration of hydrogen is greater than what is needed for complete reaction, the concentration of unreacted hydrogen in the reaction mixture would be 0.200 M − 0.155 M = 0.045 M. The equilibrium constant for the forward reaction is very large, so the equilibrium constant for the reverse reaction must be very small. The problem then is identical to that in Example 14.5.5. If we define −x as the change in the ethane concentration for the reverse reaction, then the change in the ethylene and hydrogen concentrations is +x. The final equilibrium concentrations are the sums of the concentrations for the forward and reverse reactions.

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

IACE	$[H_{2(g)}]$	$[C_2H_{4(g)}]$	$[C_2H_{6(g)}]$
Initial	0.200	0.155	0
Assuming 100% reaction	0.045	0	0.155
Change	+x	+x	−x
Final	(0.045 + x)	(0 + x)	(0.155 − x)

B Substituting values into the equilibrium constant expression,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18}$$

Once again, the magnitude of the equilibrium constant tells us that the equilibrium will lie far to the right as written, so the reverse reaction is negligible. Thus x is likely to be very small compared with either 0.155 M or 0.045 M, and the equation can be simplified [(0.045 + x) = 0.045 and (0.155 − x) = 0.155] as follows:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18}$$

$$x = 3.6 \times 10^{-19}$$

C The small x value indicates that our assumption concerning the reverse reaction is correct, and we can therefore calculate the final concentrations by evaluating the expressions from the last line of the table:

- $[C_2H_6]_f = (0.155 - x)\ M = 0.155\ M$
- $[C_2H_4]_f = x\ M = 3.6 \times 10^{-19} M$
- $[H_2]_f = (0.045 + x)\ M = 0.045\ M$

We can verify our calculations by substituting the final concentrations into the equilibrium constant expression:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

This K value agrees with our initial value at the beginning of the example.

? Exercise 14.5.6

Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

with $K_p = 4.0 \times 10^{31}$ at 47°C. If a mixture of 0.257 M H_2 and 0.392 M Cl_2 is allowed to equilibrate at 47°C, what is the equilibrium composition of the mixture?

Answer

$$[H_2]_f = 4.8 \times 10^{-32}\ M$$

$$[Cl_2]_f = 0.135\ M$$

$$[HCl]_f = 0.514\ M$$

Summary

Various methods can be used to solve the two fundamental types of equilibrium problems:

1. those in which we calculate the concentrations of reactants and products at equilibrium and
2. those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture.

When an equilibrium constant is calculated from equilibrium concentrations, molar concentrations or partial pressures are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

14.6: Reaction Directions (Empirical Explanation)

Learning Objectives

- To predict in which direction a reaction will proceed.
- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier’s principle

We previously saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

The Reaction Quotient

To determine whether a system has reached equilibrium, chemists use a quantity called the Reaction Quotient (Q). The expression for the Reaction Quotient has precisely the same form as the equilibrium constant expression from the Law of Mass Action, except that Q may be derived from a set of values measured at any time during the reaction of any mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:

$$aA + bB \rightarrow cC + dD \tag{14.6.1}$$

the Reaction Quotient is defined as follows:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{14.6.2}$$

To understand how information is obtained using a Reaction Quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,

$$\mathrm{N_2O_4(g) \rightleftharpoons 2\,NO_2(g)}. \tag{14.6.3}$$

For this reaction, $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

$$Q = \frac{[NO_2]^2}{[N_2O_4]} \tag{14.6.4}$$

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of Q were calculated for each. Each experiment begins with different proportions of product and reactant:

Table 14.6.1: Three Conditions of the dissociation of dinitrogen tetroxide to nitrogen dioxide (Equation 14.6.1)

Experiment	$[NO_2]\ (M)$	$[N_2O_4]\ (M)$	$Q = \dfrac{[NO^2]^2}{[N^2O^4]}$
1	0	0.0400	$\dfrac{0^2}{0.0400} = 0$
2	0.0600	0	$\dfrac{(0.0600)^2}{0} = \text{undefined}$
3	0.0200	0.0600	$\dfrac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$

As these calculations demonstrate, Q can have any numerical value between 0 and infinity (undefined); that is, Q can be greater than, less than, or equal to K.

Comparing the magnitudes of Q and K enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes Q

approach K. If $Q=K$, for example, then the system is already at equilibrium, and no further change in the composition of the system will occur unless the conditions are changed. If $Q<K$, then the ratio of the concentrations of products to the concentrations of reactants is less than the ratio at equilibrium. Therefore, the reaction will proceed to the right as written, forming products at the expense of reactants. Conversely, if $Q>K$, then the ratio of the concentrations of products to the concentrations of reactants is greater than at equilibrium, so the reaction will proceed to the left as written, forming reactants at the expense of products. These points are illustrated graphically in Figure 14.6.1.

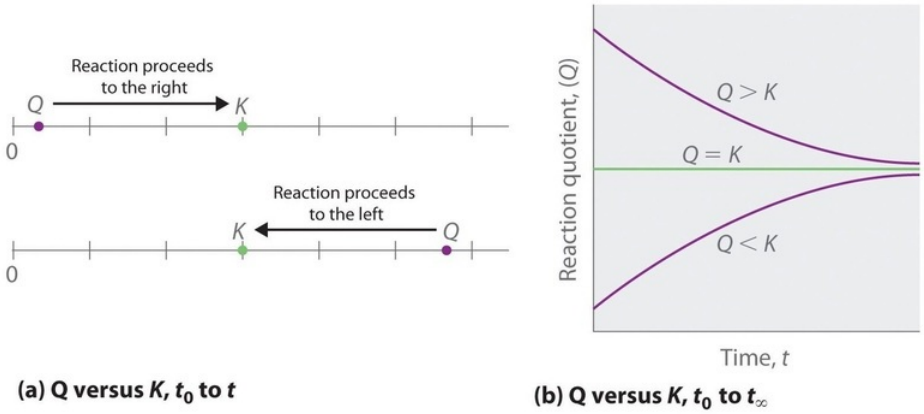


Figure 14.6.1: Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K.(a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K. (b) The change in the composition of a system with time is illustrated for systems with initial values of $Q>K$, $Q<K$, and $Q=K$.

> If $Q<K$, the reaction will proceed to the right as written. If $Q>K$, the reaction will proceed to the left as written. If $Q=K$, then the system is at equilibrium.

✓ Example 14.6.1: steam-reforming

At elevated temperatures, methane (CH_4) reacts with water to produce hydrogen and carbon monoxide in what is known as a steam-reforming reaction:

$$\mathrm{CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\,H_2(g)}$$

$K=2.4\times10^{-4}$ at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If 1.2×10^{-2} mol of CH_4, 8.0×10^{-3} mol of H_2O, 1.6×10^{-2} mol of CO, and 6.0×10^{-3} mol of H_2 are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and H_2 or to the left to form CH_4 and H_2O?

Given: balanced chemical equation, K, amounts of reactants and products, and volume

Asked for: direction of reaction

Strategy:

A. Calculate the molar concentrations of the reactants and the products.
B. Use Equation 14.6.2 to determine Q. Compare Q and K to determine in which direction the reaction will proceed.

Solution:

A: We must first find the initial concentrations of the substances present. For example, we have $1.2\times10^{-2} mol$ of CH_4 in a 2.0 L container, so

$$\begin{aligned}[CH_4] &= \frac{1.2\times10^{-2} mol}{2.0\ L} \\ &= 6.0\times10^{-3} M\end{aligned}$$

We can calculate the other concentrations in a similar way:

- $[H_2O] = 4.0 \times 10^{-3} M$,
- $[CO] = 8.0 \times 10^{-3} M$, and
- $[H_2] = 3.0 \times 10^{-3} M$.

B: We now compute Q and compare it with K:

$$\begin{aligned} Q &= \frac{[CO][H_2]^3}{[CH_4][H_2O]} \\ &= \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})} \\ &= 9.0 \times 10^{-6} \end{aligned}$$

Because $K = 2.4 \times 10^{-4}$, we see that $Q < K$. Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming H_2 and CO at the expense of H_2O and CH_4.

? Exercise 14.6.1

In the water–gas shift reaction introduced in Example 14.6.1, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

$K = 0.64$ at 900 K. If 0.010 mol of both CO and H_2O, 0.0080 mol of CO_2, and 0.012 mol of H_2 are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

Answer

$Q = 0.96$ (Q > K), so the reaction will proceed to the left, and CO and H_2O will form.

Predicting the Direction of a Reaction with a Graph

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which $Q = K$. Such a graph allows us to predict what will happen to a reaction when conditions change so that Q no longer equals K, such as when a reactant concentration or a product concentration is increased or decreased.

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:

$$PbCO_3(s) \rightleftharpoons PbO(s) + CO_2(g) \tag{14.6.5}$$

Because $PbCO_3$ and PbO are solids, the equilibrium constant is simply $K = [CO_2]$. At a given temperature, therefore, any system that contains solid $PbCO_3$ and solid PbO will have exactly the same concentration of CO_2 at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure 14.6.2, which shows a plot of $[CO_2]$ versus the amount of $PbCO_3$ added. Initially, the added $PbCO_3$ decomposes completely to CO_2 because the amount of $PbCO_3$ is not sufficient to give a CO_2 concentration equal to K. Thus the left portion of the graph represents a system that is not at equilibrium because it contains only CO2(g) and PbO(s). In contrast, when just enough $PbCO_3$ has been added to give $[CO_2] = K$, the system has reached equilibrium, and adding more $PbCO_3$ has no effect on the CO_2 concentration: the graph is a horizontal line. Thus any CO_2 concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough $PbCO_3$ and PbO are present. For example, the point labeled A in Figure 14.6.2 lies above the horizontal line, so it corresponds to a $[CO_2]$ that is greater than the equilibrium concentration of CO_2 (Q > K). To reach equilibrium, the system must decrease $[CO_2]$, which it can do only by reacting CO_2 with solid PbO to form solid $PbCO_3$. Thus the reaction in Equation 14.6.5 will proceed to the left as written, until $[CO_2] = K$. Conversely, the point labeled B in Figure 14.6.2 lies below the horizontal line, so it corresponds to a $[CO_2]$ that is less than the equilibrium concentration of CO_2 (Q < K). To reach equilibrium, the system must increase $[CO_2]$, which it can do only by decomposing solid $PbCO_3$ to form CO_2 and solid PbO. The reaction in Equation 14.6.5 will therefore proceed to the right as written, until $[CO_2] = K$.

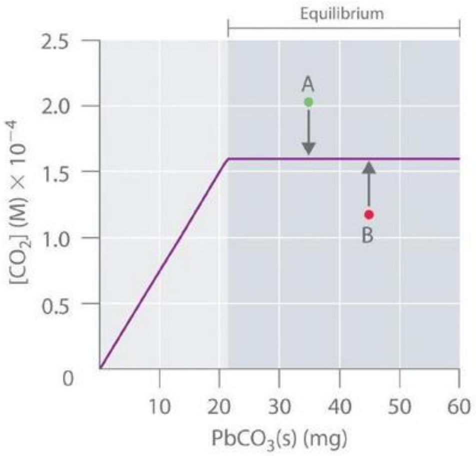


Figure 14.6.2: The Concentration of Gaseous CO_2 in a Closed System at Equilibrium as a Function of the Amount of Solid $PbCO_3$ Added. Initially the concentration of CO2(g) increases linearly with the amount of solid $PbCO_3$ added, as $PbCO_3$ decomposes to CO2(g) and solid PbO. Once the CO_2 concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $PbCO_3$ has no effect on $[CO_2]$, as long as the temperature remains constant.

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:

$$\mathrm{CdO(s)} + \mathrm{H_2(g)} \rightleftharpoons \mathrm{Cd(s)} + \mathrm{H_2O(g)} \tag{14.6.6}$$

and the equilibrium constant K is $[H_2O]/[H_2]$. If $[H_2O]$ is doubled at equilibrium, then [H2] must also be doubled for the system to remain at equilibrium. A plot of $[H_2O]$ versus $[H_2]$ at equilibrium is a straight line with a slope of K (Figure 14.6.3). Again, only those pairs of concentrations of H_2O and H_2 that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a nonequilibrium state. In such cases, the reaction in Equation 14.6.6 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point A in Figure 14.6.3 lies below the line, indicating that the $[H_2O]/[H_2]$ ratio is less than the ratio of an equilibrium mixture (Q < K). Thus the reaction in Equation 14.6.6 will proceed to the right as written, consuming H_2 and producing H_2O, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point B in Figure 14.6.3 lies above the line, indicating that the $[H_2O]/[H_2]$ ratio is greater than the ratio of an equilibrium mixture (Q > K). Thus the reaction in Equation 14.6.6 will proceed to the left as written, consuming H_2O and producing H_2, which causes the concentration ratio to move down and to the right toward the equilibrium line.

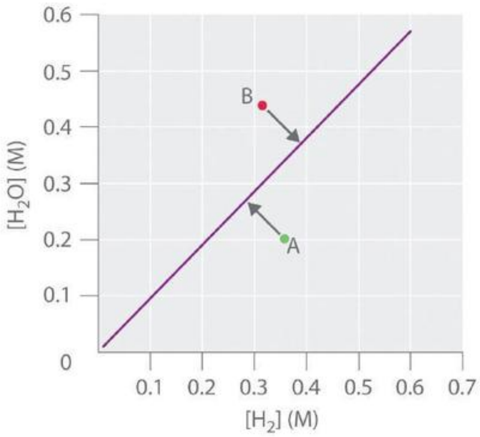


Figure 14.6.3: The Concentration of Water Vapor versus the Concentration of Hydrogen for the $CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)}$ System at Equilibrium. For any equilibrium concentration of $H_2O_{(g)}$, there is only one equilibrium concentration of H2(g). Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]$ at equilibrium requires a large $[H_2]$ and vice versa. In this case, the slope of the line is equal to K.

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:

$$NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)} \tag{14.6.7}$$

For this system, K is equal to the product of the concentrations of the two products: $[NH_3][HI]$. If we double the concentration of NH3, the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure 14.6.4. As a result, for a given concentration of either HI or NH_3, only a single equilibrium composition that contains equal concentrations of both NH_3 and HI is possible, for which $[NH_3] = [HI] = K^{1/2}$. Any point that lies below and to the left of the equilibrium curve (such as point A in Figure 14.6.4) corresponds to $Q < K$, and the reaction in Equation 14.6.7 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point B in Figure 14.6.4) corresponds to $Q > K$, and the reaction in Equation 14.6.7 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

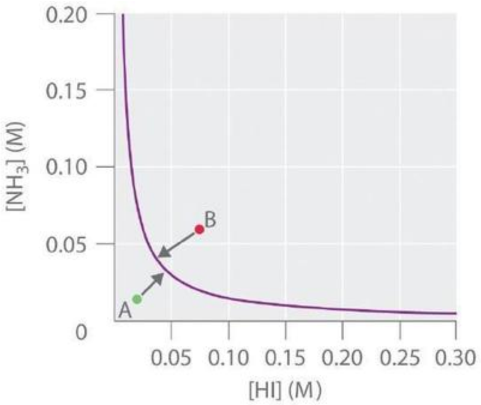


Figure 14.6.4: The Concentration of $NH_{3(g)}$ versus the Concentration of $HI_{(g)}$ for the $NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)}$ System at Equilibrium. Only one equilibrium concentration of $NH_{3(g)}$ is possible for any given equilibrium concentration of HI(g). In this case, the two are inversely proportional. Thus a large $[HI]$ at equilibrium requires a small $[NH_3]$ at equilibrium and vice versa.

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_p). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

Video 14.6.1: See www.youtube.com/watch?v=pnU7ogsgUW8 to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

$$2\,NO_{(g)} + O_{2(g)} \rightleftharpoons 2\,NO_{2(g)} \tag{14.6.8}$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \tag{14.6.9}$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the Reaction Quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \quad \Delta H = -9.4\text{ kJ (exothermic)} \tag{14.6.10}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) + \text{heat} \tag{14.6.11}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between NO_2 and N_2O_4 in this reaction

$$N_2O_{4(g)} \rightleftharpoons 2\,NO_{2(g)} \quad \Delta H = 57.20\text{ kJ} \tag{14.6.12}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\text{heat} + N_2O_{4(g)} \rightleftharpoons 2\,NO_{2(g)} \tag{14.6.13}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown color to fade.

Temperature is Neither a Reactant nor Product

It is not uncommon that textbooks and instructors to consider heat as a independent "species" in a reaction. While this is rigorously incorrect because one cannot "add or remove heat" to a reaction as with species, it serves as a convenient mechanism to predict the shift of reactions with changing temperature. For example, if heat is a "reactant" ($\Delta H > 0$), then the reaction favors the formation of products at elevated temperature. Similarly, if heat is a "product" ($\Delta H < 0$), then the reaction favors the formation of reactants. A more accurate, and hence preferred, description is discussed below.

Example 14.6.2: Steam Reforming of Methane

The commercial production of hydrogen is carried out by treating natural gas with steam at high temperatures and in the presence of a catalyst ("steam reforming of methane"):

$$\mathrm{CH_4 + H_2O \rightleftharpoons CH_3OH + H_2}$$

Given the following boiling points: CH_4 (methane) = –161°C, H_2O = 100°C, CH_3OH = 65°, H_2 = –253°C, predict the effects of an increase in the total pressure on this equilibrium at 50°, 75° and 120°C.

Solution

To identify the influence of changing pressure on the three reaction conditions, we need to identify the correct reaction including the phase of each reactant and product. Calculate the change in the moles of gas for each process:

Temperature

Equation
Δn_g
shift
50° $[\mathrm{CH_4(g) + H_2O(l) \rightarrow CH_3OH(l) + H_2(g)}$ 0 none 75° $\mathrm{CH_4(g) + H_2O(l) \rightarrow CH_3OH(g) + H_2(g)}$ +1 to left 120°
$\mathrm{CH_4(g) + H_2O(g) \rightarrow CH_3OH(g) + H_2(g)}$ 0 none

Exercise 14.6.2

What will happen to the equilibrium when the volume of the system is decreased?

$$\mathrm{2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)}$$

Answer

> Decreasing the volume leads to an increase in pressure which will cause the equilibrium to shift towards the side with fewer moles. In this reaciton, there are three moles on the reactant side and two moles on the product side, so the new equilibrium will shift towards the products (to the right).

Summary

The Reaction Quotient (Q) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction. Reaction Quotient:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The Reaction Quotient (Q or Q_p) has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium, $Q = K$. Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium.

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Footnotes

1. 1 Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle

when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium

concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress

change to a reaction's conditions that may cause a shift in the equilibrium

Contributors and Attributions

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14.7: Reaction Directions (Thermodynamic Explanation)

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously:

- $\Delta S_{univ} > 0$ (2nd law of thermodynamics),
- $\Delta G_{sys} < 0$ (Gibbs Energy version), and
- the relative magnitude of the reaction quotient Q versus the equilibrium constant K.

Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table 14.7.1 summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table 14.7.1: Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
$Q < K$	$Q = K$	$Q > K$
*Spontaneous in the reverse direction.		

Because all three criteria assess the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the standard free energy of reaction (ΔG°) and the equilibrium constant (K).

Free Energy and the Equilibrium Constant

Because ΔH° and ΔS° determine the magnitude of ΔG° and because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG° and vice versa. "Free Energy", ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. The general relationship can be shown as follow (derivation not shown):

$$\Delta G = V\Delta P - S\Delta T \tag{14.7.1}$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation 14.7.1 simplifies to

$$\Delta G = V\Delta P \tag{14.7.2}$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the V in Equation 14.7.2 by nRT/P (where n is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f, respectively):

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P \tag{14.7.3}$$

$$= nRT\frac{\Delta P}{P} = nRT\ln\left(\frac{P_\text{f}}{P_\text{i}}\right) \tag{14.7.4}$$

If the initial state is the standard state with $P_i = 1$ atm, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G^{\circ} = nRT \ln P \tag{14.7.5}$$

This can be rearranged as follows:

$$G = G^{\circ} + nRT \ln P \tag{14.7.6}$$

As you will soon discover, Equation 14.7.6 allows us to relate ΔG^o and K_p. Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA + bB \rightleftharpoons cC + dD \tag{14.7.7}$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

$$\Delta G = \sum_m G_{products} - \sum_n G_{reactants} \tag{14.7.8}$$

$$= (cG_C + dG_D) - (aG_A + bG_B) \tag{14.7.9}$$

Substituting Equation 14.7.6 for each term into Equation 14.7.9,

$$\Delta G = [(cG^o_C + cRT \ln P_C) + (dG^o_D + dRT \ln P_D)] - [(aG^o_A + aRT \ln P_A) + (bG^o_B + bRT \ln P_B)] \tag{14.7.10}$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^{\circ} + RT \ln \left(\frac{P^c_{\mathrm{C}} P^d_{\mathrm{D}}}{P^a_{\mathrm{A}} P^b_{\mathrm{B}}} \right) \tag{14.7.11}$$

$$= \Delta G^{\circ} + RT \ln Q \tag{14.7.12}$$

where ΔG° indicates that all reactants and products are in their standard states. For gases at equilibrium ($Q = K_p$,), and as you've learned in this chapter, $\Delta G = 0$ for a system at equilibrium. Therefore, we can describe the relationship between ΔG^o and K_p for gases as follows:

$$0 = \Delta G^{\circ} + RT \ln K_p \tag{14.7.13}$$

$$\Delta G^{\circ} = -RT \ln K_p \tag{14.7.14}$$

If the products and reactants are in their standard states and ΔG° < 0, then K_p > 1, and products are favored over reactants. Conversely, if ΔG° > 0, then K_p < 1, and reactants are favored over products. If ΔG° = 0, then $K_p = 1$, and neither reactants nor products are favored: the system is at equilibrium.

> *For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.*

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of Q), equilibrium is established when the system's free energy is minimized (Figure 14.7.3). If a system is present with reactants and products present in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

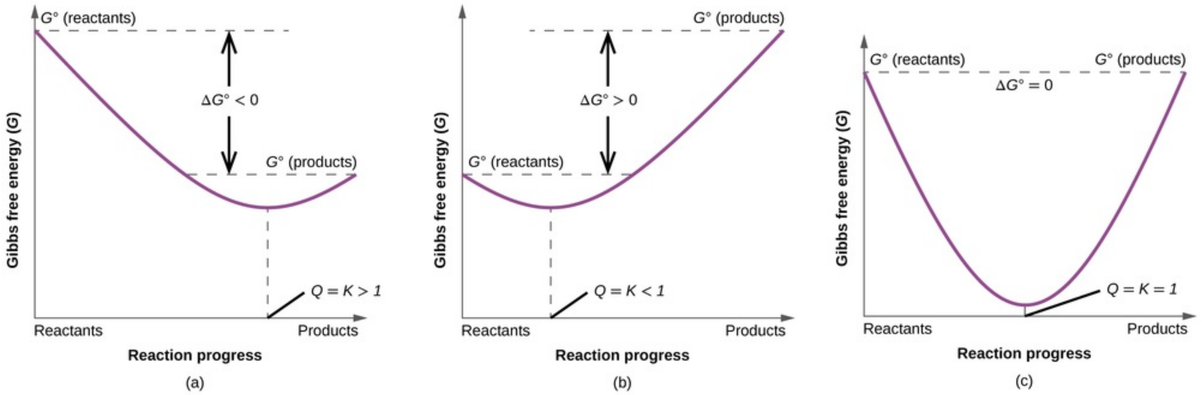

Figure 14.7.1: These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium. (CC BY 4.0; OpenStax).

Example 14.7.2

ΔG^o is −32.7 kJ/mol of N_2 for the reaction

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions:

- P_{N_2} = 2.00 atm,
- P_{H_2} = 7.00 atm,
- P_{NH_3} = 0.021 atm,
- and T = 100°C.

Does the reaction favor products or reactants?

Given: balanced chemical equation, partial pressure of each species, temperature, and ΔG°

Asked for: whether products or reactants are favored

Strategy:

A. Using the values given and Equation 14.7.12, calculate Q.
B. Substitute the values of ΔG° and Q into Equation 14.7.12to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG° and ΔG under nonstandard conditions is given in Equation 14.7.12. Substituting the partial pressures given, we can calculate Q:

$$Q = \frac{P^2_{NH_3}}{P_{N_2}P^3_{H_2}} = \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7}$$

B Substituting the values of ΔG° and Q into Equation 14.7.12,

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT\ln Q \\ &= -32.7\text{ kJ} + \left[(8.314\text{ J/K})(373\text{ K})\left(\frac{1\text{ kJ}}{1000\text{ J}}\right)\ln(6.4\times10^{-7})\right] \\ &= -32.7\text{ kJ} + (-44\text{ kJ}) \\ &= -77\text{ kJ/mol of }N_2\end{aligned}$$

Because ΔG < 0 and Q < 1.0, the reaction is spontaneous to the right as written, so products are favored over reactants.

? Exercise 14.7.2

Calculate ΔG for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: T = 50°C, P_{NO} = 0.0100 atm, P_{O_2} = 0.200 atm, and P_{NO_2} = 1.00 × 10^{-4} atm. The value of ΔG° for this reaction is −72.5 kJ/mol of O_2. Are products or reactants favored?

Answer

−92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written, so products are favored.

✓ Example 14.7.3

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C. ΔG^o for this reaction is −32.7 kJ/mol of N_2.

Given: balanced chemical equation from Example 14.7.2, ΔG°, and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG° and T (in kelvin) into Equation 14.7.14to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution

In Example 10, we used tabulated values of ΔG°_f to calculate ΔG° for this reaction (−32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 14.7.14,

$$\Delta G^\circ = -RT \ln K_p$$

$$\frac{-\Delta G^\circ}{RT} = \ln K_p$$

Inserting the value of ΔG° and the temperature (25°C = 298 K) into this equation,

$$\ln K_p = -\frac{(-32.7\ \text{kJ})(1000\ \text{J/kJ})}{(8.314\ \text{J/K})(298\ \text{K})} = 13.2$$

$$K_p = 5.4 \times 10^5$$

Thus the equilibrium constant for the formation of ammonia at room temperature is favorable. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

? Exercise 14.7.3

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. ΔG° for this reaction is −70.5 kJ/mol of O_2.

Answer

2.2 × 10^{12}

Although K_p is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant K is defined in terms of the concentrations of the reactants and the products. We described the relationship between the numerical magnitude of \(K_p\) and K previously and showed that they are related:

$$K_p = K(RT)^{\Delta n} \tag{14.7.15}$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 14.7.14can be written in a more general form:

$$\Delta G^\circ = -RT \ln K \tag{14.7.16}$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 14.7.16 for the difference between K_p and K. Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of **activities** or **fugacities** in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

Combining Equations 14.7.16 with $\Delta G^o = \Delta H^o - T\Delta S^o$ provides insight into how the components of ΔG° influence the magnitude of the equilibrium constant:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K \tag{14.7.17}$$

Notice that K becomes larger as ΔS° becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as ΔH° decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

> *The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder and seek the lowest energy state possible.*

Temperature Dependence of the Equilibrium Constant

The fact that ΔG° and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 14.7.17, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{14.7.18}$$

Assuming ΔH° and ΔS° are temperature independent, for an exothermic reaction (ΔH° < 0), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction (ΔH° > 0), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 14.7.18agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 14.7.18 also shows that the magnitude of ΔH° dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS° affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH° for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS°. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying Equation 14.7.18gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \tag{14.7.19}$$

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \tag{14.7.20}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{14.7.21}$$

Thus calculating ΔH° from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH° and ΔS° are independent of temperature. Equation 14.7.21is often referred to as the **van 't Hoff equation** after Dutch chemist Jacobus Henricus van 't Hoff in 1884 in his book Études de Dynamique chimique (Studies in dynamic chemistry).

✓ Example 14.7.4

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C was calculated to be K_p = 5.4 × 10^5 in Example 14.7.2 What is K_p at 500°C? (Use the data from Example 14.7.1)

Given: balanced chemical equation, ΔH°, initial and final T, and K_p at 25°C

Asked for: K_p at 500°C

Strategy:

Convert the initial and final temperatures to kelvin. Then substitute appropriate values into Equation 14.7.21to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of ΔH° for the reaction obtained using Hess's law is −91.8 kJ/mol of N_2. If we set T_1 = 25°C = 298 K and T_2 = 500°C = 773 K, then from Equation 14.7.21we obtain the following:

$$\begin{aligned} \ln \frac{K_2}{K_1} &= \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \\ &= \frac{(-91.8\text{ kJ})(1000\text{ J/kJ})}{8.314\text{ J/K}}\left(\frac{1}{298\text{ K}}-\frac{1}{773\text{ K}}\right) = -22.8 \\ \frac{K_2}{K_1} &= 1.3\times10^{-10} \\ K_2 &= (5.4\times10^5)(1.3\times10^{-10}) = 7.0\times10^{-5} \end{aligned}$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

? Exercise 14.7.4

The equilibrium constant for the reaction of NO with O_2 to give NO_2 at 25°C is $K_p = 2.2 \times 1012$. Use the ΔH^o_f values in the exercise in Example 14.7.4to calculate K_p for this reaction at 1000°C.

Answer

5.6 × 10^{-4}

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial pressures of the reactants and products, which gives us a relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If ΔG° < 0, then K or K_p > 1, and products are favored over reactants. If ΔG° > 0, then K or K_p < 1, and reactants are favored over products. If ΔG° = 0, then K or K_p = 1, and the system is at equilibrium. We can use the measured equilibrium constant K at one temperature and ΔH° to estimate the equilibrium constant for a reaction at any other temperature.

Contributors and Attributions

- Mike Blaber (Florida State University)
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14.8: Distribution of a Single Species between Immiscible Phases - Extraction and Separation

A partitioning of a compound exist between a mixture of two immiscible phases at equilibrium, which is a measure of the difference in solubility of the compound in these two phases. If one of the solvents is a gas and the other a liquid, the "gas/liquid partition coefficient" is the same as the dimensionless form of the Henry's law constant. A solute can partition when one or both solvents is a solid (e.g., solid solution).

Liquid-Liquid Extractions

We call the process of moving a species from one phase to another phase an **extraction**. Simple extractions are particularly useful for separations where only one component has a favorable partition coefficient. Several important separation techniques are based on a simple extraction, including liquid–liquid, liquid–solid, solid–liquid, and gas–solid extractions. The most important group of separation techniques uses a selective partitioning of the solute between two immiscible phases. If we bring a phase containing a solute, S, into contact with a second phase, the solute partitions itself between the two phases, as shown by the following equilibrium reaction.

$$\mathrm{S_{phase\,1}} \rightleftharpoons \mathrm{S_{phase\,2}} \tag{14.8.1}$$

The equilibrium constant for this equlibrium is

$$K_{\mathrm{D}}=\frac{[\mathrm{S_{phase\ 2}}]}{[\mathrm{S_{phase\ 1}}]} \tag{14.8.2}$$

is called the distribution constant or **partition coefficient**. If K_D is sufficiently large, then the solute moves from phase 1 to phase 2. The solute remains in phase 1 if the partition coefficient is sufficiently small. When we bring a phase containing two solutes into contact with a second phase, if K_{D} is favorable for only one of the solutes a separation of the solutes is possible. The physical states of the phases are identified when describing the separation process, with the phase containing the sample listed first. For example, if the sample is in a liquid phase and the second phase is a solid, then the separation involves liquid–solid partitioning.

It often happens that two immiscible liquid phases are in contact, one of which contains a solute. How will the solute tend to distribute itself between the two phases? One’s first thought might be that some of the solute will migrate from one phase into the other until it is distributed equally between the two phases, since this would correspond to the maximum dispersion (randomness) of the solute. This, however, does not take into the account the differing solubilities the solute might have in the two liquids; if such a difference does exist, the solute will preferentially migrate into the phase in which it is more soluble (Figure 14.8.1).

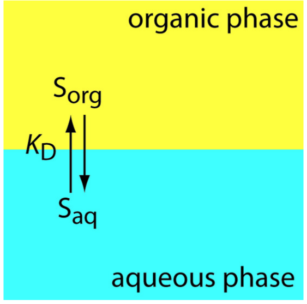

Figure 14.8.1: Scheme for a simple liquid–liquid extraction in which the solute’s partitioning depends only on the K_{D} equilibrium.

Biomagnification

The transport of substances between different phases is of immense importance in such diverse fields as pharmacology and environmental science. For example, if a drug is to pass from the aqueous phase with the stomach into the bloodstream, it must pass through the lipid (oil-like) phase of the epithelial cells that line the digestive tract. Similarly, a pollutant such as a pesticide residue that is more soluble in oil than in water will be preferentially taken up and retained by marine organism, especially fish, whose bodies contain more oil-like substances; this is basically the mechanism whereby such residues as DDT can undergo *biomagnification* as they become more concentrated at higher levels within the food chain. For this reason, environmental

> regulations now require that oil-water distribution ratios be established for any new chemical likely to find its way into natural waters. The standard “oil” phase that is almost universally used is octanol, $C_8H_{17}OH$.

In preparative chemistry it is frequently necessary to recover a desired product present in a reaction mixture by extracting it into another liquid in which it is more soluble than the unwanted substances. On the laboratory scale this operation is carried out in a **separatory funnel** as shown below. The two immiscible liquids are poured into the funnel through the opening at the top. The funnel is then shaken to bring the two phases into intimate contact, and then set aside to allow the two liquids to separate into layers, which are then separated by allowing the more dense liquid to exit through the stopcock at the bottom.

Figure 14.8.2: A separatory funnel with two solvents.

If the distribution ratio is too low to achieve efficient separation in a single step, it can be repeated; there are automated devices that can carry out hundreds of successive extractions, each yielding a product of higher purity. In these applications our goal is to exploit the Le Chatelier principle by repeatedly upsetting the phase distribution equilibrium that would result if two phases were to remain in permanent contact.

Video 14.8.1: How to perform a liquid-liquid extraction using a separating funnel.

✓ Example 14.8.1

The distribution ratio for iodine between water and carbon disulfide is 650. Calculate the concentration of I_2 remaining in the aqueous phase after 50.0 mL of 0.10M I_2 in water is shaken with 10.0 mL of CS_2.

Solution

The equilibrium constant is

$$K_d = \frac{C_{CS_2}}{C_{H_2O}} = 650$$

Let m_1 and m_2 represent the numbers of millimoles of solute in the water and CS_2 layers, respectively. K_d can then be written as (m_2/10 mL) ÷ (m_1/50 mL) = 650. The number of moles of solute is (50 mL) × (0.10 mmol mL^{-1}) = 5.00 mmol, and mass conservation requires that m_1 + m_2 = 5.00 mmol, so m_2 = (5.00 – m_1) mmol and we now have only the single unknown m_1. The equilibrium constant then becomes

$$\frac{(5.00 - m_1)\, mmol/10\, mL}{m_1\, mmol/50\, mL} = 650$$

Simplifying and solving for m_1 yields

$$\frac{(0.50 - 0.1)m_1}{0.02\, m_1} = 650$$

with m_1 = 0.0382 mmol.

The concentration of solute in the water layer is (0.0382 mmol) / (50 mL) = **0.000763 M**, showing that almost all of the iodine has moved into the CS_2 layer.

Chromatographic Separations

In an extraction, the sample is one phase and we extract the analyte or the interferent into a second phase. We also can separate the analyte and interferents by continuously passing one sample-free phase, called the mobile phase, over a second sample-free phase that remains fixed or stationary. The sample is injected into the mobile phase and the sample’s components partition themselves between the mobile phase and the stationary phase. Those components with larger partition coefficients are more likely to move into the stationary phase, taking a longer time to pass through the system. This is the basis of all chromatographic separations. Chromatography provides both a separation of analytes and interferents, and a means for performing a qualitative or quantitative analysis for the analyte.

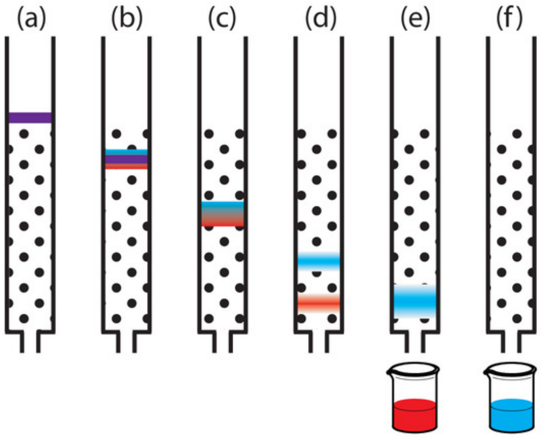

Figure 14.8.3: Progress of a column chromatographic separation of a two-component mixture. In (a) the sample is layered on top of the stationary phase. As mobile phase passes through the column, the sample separates into two solute bands (b–d). In (e) and (f), we collect each solute as it elutes from the column.

Of the two methods for bringing the stationary phase and the mobile phases into contact, the most important is column chromatography. In this section we develop a general theory that we may apply to any form of column chromatography. Figure 14.8.3 provides a simple view of a liquid–solid column chromatography experiment. The sample is introduced at the top of the column as a narrow band. Ideally, the solute’s initial concentration profile is rectangular (Figure 14.8.1a). As the sample moves down the column the solutes begin to separate (Figures 14.8.1b, c), and the individual solute bands begin to broaden and develop a Gaussian profile. If the strength of each solute’s interaction with the stationary phase is sufficiently different, then the solutes separate into individual bands (Figure 14.8.1d).

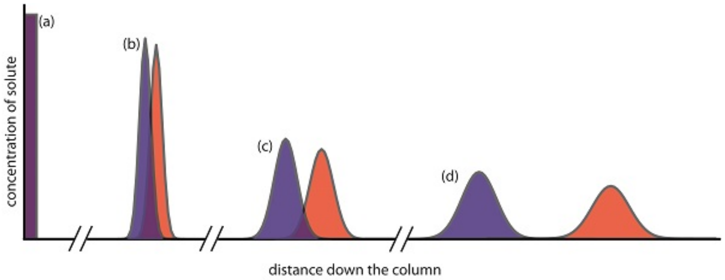

Figure 14.8.4: An alternative view of the separation in Figure 14.8.3 showing the concentration of each solute as a function of distance down the column.

We can follow the progress of the separation either by collecting fractions as they elute from the column (Figure 14.8.4), or by placing a suitable detector at the end of the column. A plot of the detector's response as a function of elution time, or as a function of the volume of mobile phase, is known as a **chromatogram** (Figure 14.8.5), and consists of a peak for each solute.

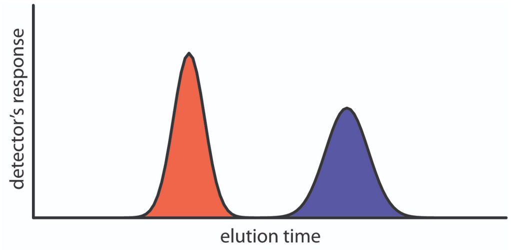

Figure 14.8.5: Chromatogram for the separation shown in Figure 14.8.3 showing the detector's response as a function of the elution time.

Contributors and Attributions

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14.E: Chemical Equilibria (Exercises)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

Q1

Write an expression for the equilibrium constant K_c for each reaction below.

a. $2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$
b. $N_2H_4(g) + 3\,O_2(g) \rightleftharpoons 2\,NO_2(g) + H_2O(g)$
c. $O_3(g) + H_2O(l) \rightleftharpoons H_2(g) + 2\,O_2(g)$

Solution

For a general reaction $aA + bB \rightleftharpoons cC + dD$ then Law of Mass Action argues we can construct an equilibrium constant thusly

$$K_c = \frac{[C]c[D]d}{[A]a[B]b}$$

This is the general equations to substitute the reactants and product concentrations (with coefficients as exponents).

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

a. $K_c = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$
b. $K_c = \dfrac{[H_2O][NO_2]^2}{[N_2H_4][O_2]^3}$
c. $K_c = \dfrac{[O_2]^2[H_2]}{[O_3]}$

Note that for part c, $H_2O(l)$ is not included because pure solids and liquids are not included in the equilibrium constant.

Q3

Gaseous chlorine reacts with water vapor to form hydrogen chloride and oxygen gas. Write down the equilibrium expression (K_p) for the reaction.

Solution

First, a balanced reaction is constructed to ensure the equilibrium expression will be correctly states.

$$2\,Cl_2 + 2\,H_2O \rightleftharpoons 4\,HCl + O_2$$

Equilibrium expression K_p is as follows:

$$K_p = \frac{p^4_{HCl}\,p_{O_2}}{p^2_{Cl_2}\,p^2_{H_2O}}$$

Q11

For each thermodynamics equilibrium expressions outlined below, determine one possible chemical reaction related to each.

a. $$K = \frac{a\{CO\}^2}{a\{CO_2\}}$$

b. $$K = \frac{a\{H_2O\}^2}{a\{H_2\}^2 a\{O_2\}}$$

c. $$K = \frac{a\{Cl_2O\}^2}{a\{Cl_2\}^2 a\{O_2\}}$$

d. $$K = \frac{a\{COCl_2\}}{a\{CO\} \cdot a\{Cl_2\}}$$

Solution

a. $$CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)$$

b. $$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g)$$

c. $$2\,Cl_2(g) + O_2(g) \rightleftharpoons 2\,Cl_2O(g)$$

d. $$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

Q15A

Based on the following data, calculate the equilibrium constant and the value of ΔG at 273 K.

a. $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$ with

- $[CO_2]_{eq} = 0.0954\,M$
- $[H_2]_{eq} = 0.0454\,M$
- $[CO]_{eq} = 0.0046\,M$
- $[H_2O]_{eq} = 0.0046\,M$

b. $2\,NO(g) + 2\,H_2(g) \rightleftharpoons N_2(g) + 2\,H_2O(g)$ with

- $[NO]_{eq} = 0.45\,M$
- $[H_2]_{eq} = 0.63\,M$
- $[N_2]_{eq} = 0.95\,M$
- $[H_2O]_{eq} = 1.3\,M$

Solution

a)

$$\begin{aligned} K &= \frac{[CO][H_2O]}{[CO_2][H_2]} \\ &= \frac{(0.0046)(0.0046)}{(0.0954)(0.0454)} \\ &= 4.9 \times 10^{-3} \end{aligned}$$

$$\Delta G = RT\ln(K) = (8.3145\,J/(K\,mol))(273\,K)\ln(4.9 \times 10^{-3}) = -12072.288\,J/mol$$

b)

$$K = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2} = \frac{[0.95][1.3]^2}{[0.45]^2[0.63]^2} = 19.98$$

$$\Delta G = RT\ln(K) = (8.3145\,J/K\,mol)(273\,K)\ln(19.98) = 6797.62\,J/mol$$

Q15B

Calculate the appropriate K value for the following reactions using the information provided. Assume that they are preformed under standard conditions (and 298.15 K).

a. $$2\,\mathrm{NO_2(g)} \rightleftharpoons 2\,\mathrm{NO(g)} + \mathrm{O_2(g)}$$

b. $$\mathrm{NH_4^+(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \mathrm{NH_3(aq)}$$

c. Jim's brother, Txeltoqlztop, goes to the bathroom only to find out that his sibling did not refill the toilet paper roll! To get revenge, Txeltoqlztop decides to fill his brother's room with carbon monoxide, via the following reaction:

$$2\,\mathrm{CH_4(g)} + 3\,\mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{CO(g)} + 4\,\mathrm{H_2O(g)}$$

Calculate the K value for this equation under standard conditions, interpret what it means in regards to the direction this equation will go, and compare it to the other two.

Solution

The core of this problem is to find the K value and understanding what information it can describe about the reaction. Since the problem provides many, many ΔG_f, it is likely that to calculate the K value, a relationship needs to be drawn from ΔG to K. This relationship is as follows:

$$\Delta G^\circ_{\text{rxn}} = -RT\ln(K_p)$$

Relevant Information obtained from the thermodynamic tables

$$\Delta G^\circ_f\ \mathrm{NO_2(g)} = 51.30\frac{\mathrm{kJ}}{\mathrm{mol}}\ \Delta G^\circ_f\ \mathrm{H_3O^+(aq)} = -103.45\frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\Delta G^\circ_f\ \mathrm{NO(g)} = 86.57\frac{\mathrm{kJ}}{\mathrm{mol}}\ \Delta G^\circ_f\ \mathrm{NH_3(aq)} = -26.5\frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\Delta G^\circ_f\ \mathrm{O_2(g)} = 0\frac{\mathrm{kJ}}{\mathrm{mol}}\ \ \Delta G^\circ_f\ \mathrm{CH_4(g)} = -50.84\frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\Delta G^\circ_f\ \mathrm{NH_4^+(aq)} = -79.37\frac{\mathrm{kJ}}{\mathrm{mol}}\ \Delta G^\circ_f\ \mathrm{CO(g)} = -137.28\frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\Delta G^\circ_f\ \mathrm{H_2O(l)} = -237.14\frac{\mathrm{kJ}}{\mathrm{mol}}\ \Delta G^\circ_f\ \mathrm{H_2O(g)} = -228.61\frac{\mathrm{kJ}}{\mathrm{mol}}$$

Note that the relationship here is between ΔG and K_p, which is:

$$K_p \approx \frac{P_{\text{products}}}{P_{\text{reactants}}}$$

Where P is partial pressure of the products or reactants. The reason this is an approximation is because the equilibrium actually measures the *activities* of the species, but by using just the partial pressures a good estimate is procured. Since the equation relating K_p and ΔG only has these two variables as unknown, once ΔG is found, algebra can find K_p. The process for utilizing Hess's Law to find state variables is outlined extensively. The values below were found using the exact same process, now for ΔG (Just in case, the Hess law formula is provided).

$$\Delta G^\circ = \sum n_{\text{products}} \times \Delta G^\circ_{f_{\text{products}}} - \sum n_{\text{reactants}} \times \Delta G^\circ_{f_{\text{reactants}}}$$

$$\Delta G^\circ(2\,\mathrm{NO_2(g)} \rightleftharpoons 2\,\mathrm{NO(g)} + \mathrm{O_2(g)}) = 70.42\ \frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\Delta G^\circ(\mathrm{NH_4^+(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \mathrm{NH_3(aq)}) = -437.93\frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\Delta G^\circ(2\,\mathrm{CH_4(g)} + 3\,\mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{CO(g)} + 4\,\mathrm{H_2O(l)}) = -1121.44\frac{\mathrm{kJ}}{\mathrm{mol}}$$

To find K, plug in the ΔG into the equation above. (Note that the solution does NOT show the conversion of the gas constant from J to kJ!!)

$$\Delta G^\circ_{\text{rxn}} = -\left(8.314\ \frac{\mathrm{J}}{\mathrm{mol\,K}}\right)(298.15\,\mathrm{K}) \times \ln(K_p)$$

$$70.54\frac{\mathrm{kJ}}{\mathrm{mol}} = -\left(8.314\frac{\mathrm{J}}{\mathrm{mol\,K}}\right)(298.15\,\mathrm{K}) \times \ln(K_p)$$

$$-\frac{70.54\,\frac{\text{kJ}}{\text{mol}}}{\left(8.314\,\frac{\text{J}}{\text{molK}}\right)(298.15\,\text{K})}=\ln(K_p)$$

$$e^{-\frac{70.54\,\frac{\text{kJ}}{\text{mol}}}{\left(8.314\,\frac{\text{J}}{\text{mol K}}\right)(298.15\,\text{K})}}=K_p$$

$$K_p\approx e^{-28.457}\approx 4.3776\times 10^{-13}$$

Thus, the K_p value for $2\,NO_2(g)\rightleftharpoons 2\,NO(g)+O_2(g)$ is a very small number!. Since the equilibrium value depicts the ratio of products to reactants at the equilibrium point, this very tiny K_p value means that the reaction will heavily favor the reactants. The third reaction where Txeltoqlztop wants to poison his brother with CO also follows the same process, and the answer is such:

$$K_p\approx e^{452}$$

e^{452} is a *really* big number! That means, while the previous reaction will stay mostly on the reactant sides, this reaction heavily favors the products side, meaning that pretty much all of the methane and oxygen that Txeltoqlztop uses will be transformed into carbon monoxide, which is all the better for him!

The same method can be applied to the aqueous reaction, but the K value calculated is K_c rather than K_p.

$$K_c\approx e^{-176.65}\approx 1.898\times 10^{-77}\ *$$

*These equilibrium constants are based solely off the calculated Gibbs energy, some of the reactions, therefore, may have actual K values much different from the ones calculated.

Abstract: use of $\Delta G^\circ_{\text{rxn}}=-RT\times\ln(K_p)$

Q15C

Use the thermodynamic data in Tables T1 and T2 to calculate the equilibrium constants for the following equations at 25°C.

a. $H_2(g)+2\,F(g)\rightleftharpoons 2\,HF(g)$
b. $FeCl_3(s)\rightleftharpoons FeCl_2(s)+Cl_2(g)$
c. $CaSO_4(s)\rightleftharpoons Ca^{2+}(aq)+SO_4^{2-}(aq)$

Solution

For each of the chemical reactions, the main equation needed is

$$\Delta G_{\text{rxn}}=-R\times T\times\ln K$$

Where R is 8.134 J K^{-1} mol^{-1} and T is equal to 298K. In order to determine the value of G$_{\text{rxn}}$, the following the reaction is needed

$$\Delta G_{\text{rxn}}=\sum nG^\circ_f(\text{products})-\sum nG^\circ_f(\text{reactants})$$

a. By looking in the tables, the ΔG of formation can be found and they are listed for each compound below

$H_2(g)$ = 203.3 J mol^{-1}, $F_2(g)$ = 62.3 J mol^{-1}, HF(g)=-275.4 J mol^{-1}

Next, these values are plugged into the second equation to the the change in Gibbs energy for the reaction

$$\Delta G_{\text{rxn}}=-275.4\ \text{J mol}^{-1}-(203.3\ \text{J mol}^{-1}+62.3\ \text{J mol}^{-1})=-514\ \text{J mol}^{-1}$$

Using the the value for the Gibbs Energy, the value of K can be determined using the first equation

$$-541\ \text{J mol}^{-1}=-8.314\ \text{J K}^{-1}\text{mol}^{-1}\times 298\,\text{K}\times\ln K$$

$$\frac{-541\ \mathrm{J\,mol^{-1}}}{-8.314\ \mathrm{J\,K^{-1}\,mol^{-1}} \times 298\,\mathrm{K}} = \ln K$$

$$K = 1.25$$

b. The ΔG of formation for the compounds are

$FeCl_3$(s) = -334.0 J mol^{-1}, $FeCl_2$(s) = -302.3 J mol^{-1}, Cl(g)=105.3 J mol^{-1}

The calculations are

$$\Delta G_{\mathrm{rxn}} = (-302.3\ \mathrm{J\,mol^{-1}} + 105.3\ \mathrm{J\,mol^{-1}}) + 334.0\ \mathrm{J\,mol^{-1}} = 137\ \mathrm{J\,mol^{-1}}$$

$$137\ \mathrm{J\,mol^{-1}} = -8.314\ \mathrm{J\,K^{-1}\,mol^{-1}} \times 298\,\mathrm{K} \times \ln K$$

$$\frac{137\ \mathrm{J\,mol^{-1}}}{-8.314\ \mathrm{J\,K^{-1}\,mol^{-1}} \times 298\,\mathrm{K}} = \ln K$$

$$K = 0.945$$

c. The ΔG of formation for the compounds are

$CaSO_4$(s)= -1322.0 J/mol, Ca^{2+}(aq) = -553.58 J/mol, SO_4^{2-}(aq) = -744.53 J/mol

The calculations are

$$\Delta G_{\mathrm{rxn}} = (-553.58\ \mathrm{J\,mol^{-1}} - 744.53\ \mathrm{J\,mol^{-1}}) + 1322.0\ \mathrm{J\,mol^{-1}} = 23.89\ \mathrm{J\,mol^{-1}}$$

$$23.89\ \mathrm{J\,mol^{-1}} = -8.314\ \mathrm{J\,K^{-1}\,mol^{-1}} \times 298\,\mathrm{K} \times \ln K$$

$$\frac{23.89\ \mathrm{J\,mol^{-1}}}{-8.314\ \mathrm{J\,K^{-1}\,mol^{-1}} \times 298\,\mathrm{K}} = \ln K$$

$$K = 0.99$$

Q17

To ignite this house on fire, you dowsed the house in some ethanol and used a combustion reaction:

$$\mathrm{C_2H_5OH(l) + O_2(g) \rightleftharpoons H_2O(l) + CO_2(g)}$$

This reaction has an equilibrium constant of K_1. If you multiply this equation by 5, will the equilibrium constant change? If so, write this new equilibrium constant, K_2, in terms of K_1.

Solution

Because:

$$K = \frac{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}}{[\mathrm{C}]^{\mathrm{c}}[\mathrm{D}]^{\mathrm{d}}}$$

If we multiply a chemical equation by a constant, the exponents of K will be multiplied by that multiple as well.

For this question, first balance this chemical equation,

$$\mathrm{C_2H_5OH(l) + 3\,O_2(g) \rightleftharpoons 3\,H_2O(l) + 2\,CO_2(g)}$$

the corresponding equilibrium constant is

$$K_1 = \frac{[\mathrm{CO_2}]^2}{[\mathrm{O_2}]^3}$$

since liquid is ignored.

When we multiply this equation by 5, the chemical equation becomes,

$$5\,C_2H_5OH(l) + 15\,O_2(g) \rightleftharpoons 15\,H_2O(l) + 10\,CO_2(g)$$

the corresponding equilibrium constant is

$$K_2 = \frac{[CO_2]^{10}}{[O_2]^{15}} = \left(\frac{[CO_2]^2}{[O_2]^3}\right)^5$$

Therefore, for this reaction, the equilibrium constant changes and $K_2 = K_1^5$.

Q21

An unknown gas B_5D_{10} reacts at room temperature and becomes $B_{10}D_{20}$, the reaction is illustrated with the equation

$$2\,B_5D_{10}(g) \rightleftharpoons B_{10}D_{20}(g)$$

At room temperature the equilibrium partial pressure of B_5D_{10} is 1.23×10^{-4} atm and that of $B_{10}D_{20}$ is 3.14×10^{-16} atm. Given these constants, what is K_p of this reaction at room temperature.

Solution

Given that we already know the partial pressures and this reaction is at equilibrium, we simply substitute the values into the equilibrium equation and solve for K_p.

$$K_p = \frac{[\text{products}]}{[\text{reactants}]}$$

$$K_p = \frac{[3.14 \times 10^{-16}]}{[1.23 \times 10^{-4}]^2} = 2.08 \times 10^{-8}$$

$$K_p = 2.08 \times 10^{-8}$$

Q23A

Suppose there exists a compound that can be found in two forms, red and blue, such that

$$X_{red} \rightleftharpoons X_{blue}$$

During equilibrium at 25.0°C, 17% of the substance is determined to be in blue form. What is the equilibrium constant for this reaction?

Solution

The equilibrium constant, K_{eq}, for the chemical equation

$$X_{red} \rightleftharpoons X_{blue}$$

can be calculated by constructing the following equation:

$$K_{eq} = \frac{[X_{blue}]}{[X_{red}]}$$

Given that 17% of the concentration is X_{blue}, that means the remaining 83% is X_{red}, which can be plugged into the equation to yield

$$K_{eq} = \frac{[0.17]}{[0.83]} = 0.205$$

which can be further reinforced by viewing it as the fact that since $K_{eq} < 1$, the concentration of products present is expected to be smaller than the concentration of reactants.

Q23B

1,2-dimethylcyclohexane can exist in both boat and chair conformation. There is equilibrium between the two forms. What is the equilibrium constant for the reaction of boat conformation to chair conformation if the molecules in the boat form are 68.7%?

Solution

$$[\mathrm{Boat}] \longrightarrow [\mathrm{Chair}]$$

Let B stand for Boat and C stand for Chair, then the equilibrium constant for this reaction is

$$K = \frac{[\mathrm{C}]}{[\mathrm{B}]}$$

For [C] and [B] here, we can use the molar concentration $c = n/V$, then

$$[\mathrm{C}] = n(\mathrm{C})/V$$

$$[\mathrm{B}] = n(\mathrm{B})/V$$

So

$$K = \frac{n(\mathrm{C})/V}{n(\mathrm{B})/V} = \frac{n(\mathrm{C})}{n(\mathrm{B})} = \frac{n(\mathrm{C})/n_{\mathrm{tot}}}{n(\mathrm{B})/n_{\mathrm{tot}}}$$

From the question, it consists only with boat and chair conformation, so $n(\mathrm{C})/n_{\mathrm{tot}} = 0.687$, and the remaining is for boat, so $n(\mathrm{B})/n_{\mathrm{tot}} = 1 - 0.687 = 0.313$.

Therefore, the equilibrium constant is

$$K = \frac{n(\mathrm{C})/n_{\mathrm{tot}}}{n(\mathrm{B})/n_{\mathrm{tot}}} = \frac{0.687}{0.313} = 2.19$$

Q28

The K_p for the following reaction is 3.0 at 1000 K.

$$\mathrm{CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)}$$

a. If the pressure in the container where the reaction occurs was initially 0.48 bar, calculate the partial pressures of $\mathrm{CO_2}$ and CO at equilibrium.
b. Calculate the percentage of $\mathrm{CO_2}$ that has been dissociated.

Solution

a)

$$\mathrm{CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)}$$

	$\mathrm{CO_2(g)}$	$\mathrm{CO(g)}$
Initial	0.48	0
Change	$-x$	$+2x$
Equilibrium	$0.48 - x$	$2x$

$$K_p = \frac{p(\mathrm{CO})^2}{p(\mathrm{CO_2})}$$

⇒

$$3 = \frac{(2x)^2}{(0.48 - x)}$$

⇒

$$4x^2 = 3(0.48 - x)$$

⇒

$$4x^2 = 1.44 - 3x$$

⇒

$$4x^2 + 3x - 1.44 = 0$$

By solving the quadratic equation, the positive value we get is

$$x = 0.33$$

Hence at equilibrium,

$$p(\text{CO}) = 2x = 0.66$$

$$p(\text{CO}_2) = 0.48 - x = 0.48 - 0.33 = 0.15\text{ bar}$$

b) For fraction that has not reacted,

$$\frac{p(\text{CO}_2(\text{final}))}{p(\text{CO}_2(\text{initial}))} \times 100\%$$

The unreacted percentage is

$$= \frac{0.15}{0.48} \times 100\% = 31.25\%$$

Hence, 68.75% of the CO_2 has reacted.

Q29

A 100.0 mL glass bulb was filled which a weighed sample of solid XO_3, where X is an unknown element. The bulb was then attached to a pressure gauge and heated to 325 K, at which, the pressure was read to be 0.891 atm. Given that all of the XO_3 in the bulb at 325 K was in the gas phase, and it also partially dissociated into $\text{O}_2(\text{g})$ and $\text{XO}(\text{g})$:

$$\text{XO}_3(\text{g}) \rightleftharpoons \text{O}_2(\text{g}) + \text{XO}(\text{g})$$

At 325 K, K_p = 3.14 for this reaction. Calculate the partial pressures of all three species in the bulb at equilibrium.

Solution

$$\text{XO}_3(\text{g}) \rightleftharpoons \text{O}_2(\text{g}) + \text{XO}(\text{g})$$

Let Y be the initial partial pressure of X_2O_5, and x is the change in partial pressure of O_2:

ICE	XO_3	O_2	XO
Initial	y	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$y - x$	x	x

The total pressure is 0.891 atm, therefore:

$$(y - x) + x + x = 0.891\text{ atm}$$

$$y + x = 0.891\text{ atm}$$

$$y = 0.891 - x$$

So the ICE table now would be:

ICE	XO_3	O_2	XO
Initial	$0.891 - x$	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.891 - 2x$	x	x

$$K_p = 3.14 = \frac{P_{XO} \cdot P_{O_2}}{P_{XO_3}} = \frac{x^2}{0.891 - 2x}$$

$$x^2 + 6.28x - 2.80 = 0$$

$$x = 0.418$$

$$P_{O_2} = P_{XO} = 0.418\text{ atm}$$

$$P_{XO_3} = 0.891 - 2(0.418) = 0.055\text{ atm}$$

Q31

The equilibrium constant K_c for the reaction

$$F_2(g) + H_2(g) \rightleftharpoons 2\,HF(g)$$

at 298 K is 5.07×10^4. Hydrogen with a partial pressure of 0.03500 atm is mixed with fluorine with a partial pressure of 0.06800 atm, and allowed to reach the equilibrium. What is the partial pressure of each of the gasses at the equilibrium?

Solution

We are looking for partial pressures of the reactants and we have starting partial pressures and a K_c value. First we need to convert K_c to K_p

$$K_p = K_c(RT)^{\Delta n_{\text{gas}}}$$

$$K_p = (5.07 \times 10^4) \times (0.0821 \times 298\text{ K})^0 = 5.07 \times 10^4$$

The equilibrium constant can be constructed from the equation given

$$K_p = \frac{[HF]^2}{[H_2][F_2]}$$

Use an ICE table to find the equilibrium partial pressures of the equilibrium

Reaction	$H_2(g)$	$F_2(g)$	$2\,HF(g)$
I	0.035	0.068	0
C	$-x$	$-x$	$+2x$
E	$0.035 - x$	$0.068 - x$	$2x$

$$5.07 \times 10^4 = \frac{[2x]^2}{[0.035 - x]^2[0.068 - x]^2}$$

Simplify the equation and solve as you wish. You can't use the quadratic formula because you end up with a degree three equation but you can put the equation into a graphing calculator and solve for x using the zero function.

$$x = 0.0286\text{ atm}$$

$$[\mathrm{HF}] = 2x = 0.0571\,\mathrm{atm}$$

$$[\mathrm{H_2}] = 0.035 - x = 0.00643\,\mathrm{atm}$$

$$[\mathrm{F_2}] = 0.068 - x = 0.0394\,\mathrm{atm}$$

Q33

At 25 °C, the equilibrium constant for the reaction below has the value of 1.7×10^{-13}:

$$\mathrm{N_2O(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{NO(g)}$$

In a container where N_2O has an initial partial pressure of 0.62 atm, O_2 has a pressure of 0.24 atm, and NO has an initial pressure of 0.08 atm, what will the partial pressure of the three gases be after reaching equilibrium at the same temperature?

Q35

The reaction:

$$2\,\mathrm{HI(g)} \rightleftharpoons \mathrm{H_2(g)} + \mathrm{I_2(g)}$$

has an equilibrium constant $K_c = 1.82 \times 10^{-2}$ at 698 K. If the reaction took place in a tank at 698 K and started off with HI having a partial pressure of 1 atm, what would the partial pressures of all the gases be at equilibrium?

Solution

First, we need to convert K_c into K_p with the equation

$$K_p = K_c(RT)^{\Delta n}$$

$$K_p = 1.82 \times 10^{-2}(0.0821\,\mathrm{L\,atm\,/\,K\,mol} \times 698\,\mathrm{K})^{2-2}$$

$$K_p = 1.82 \times 10^{-2}$$

An ICE table can also be constructed for the reaction:

$$2\,\mathrm{HI(g)} \rightleftharpoons \mathrm{H_2(g)} + \mathrm{I_2(g)}$$

ICE Table	$2\,\mathrm{HI(g)}$	$\mathrm{H_2(g)}$	$\mathrm{I_2(g)}$
Initial	1	0	0
Change	$-2x$	$+x$	$+x$
Equilibrium	$1-2x$	x	x

$$0.82 \times 10^{-2} = \frac{x^2}{1-2x}$$

$$x^2 = 1.82 \times 10^{-2} - 0.0368x$$

$$x = 0.118488$$

$$\text{partial pressure of HI} = 0.763\,\mathrm{atm}$$

$$\text{partial pressure of }\mathrm{H_2} = \text{partial pressure of }\mathrm{I_2} = 0.1189\,\mathrm{atm}$$

Q37

What is the concentration of a XY that will be found in equilibrium at room temperature, given that X_2 has a concentration of 3.14×10^{-15} M, Y_2 has a concentration of 1.23×10^{-4} M, and the K_c of the reaction is 2.22×10^{-7} M.

Solution

First we must state what the formulas for both the reaction and K_c and then we can substitute the known values and solve for the concentration of XY as an unknown variable.

$$2\,XY(g) \rightleftharpoons X_2(g) + Y_2(g)$$

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$K_c = \frac{[X_2][Y_2]}{[XY]^2} = \frac{[3.14\times10^{-15}][1.23\times10^{-4}]}{[XY]^2} = 2.22\times10^{-7}$$

$$K_c = \frac{[3.86\times10^{-19}]}{[XY]^2} = 2.22\times10^{-7}$$

$$K_c = 3.86\times10^{-19} = 2.22\times10^{-7}[XY]^2$$

$$[XY] = 1.32\times10^{-6}$$

So the concentration of XY is 1.32×10^{-6} M in equilibrium at 25ºC.

Q41

Hydrogen and oxygen gas react with each other to form gaseous water with an equilibrium constant for the reaction is $K_c = 1.33\times10^{20}$ at 1000 K.

a. Consider a system at 1000.0 K in which 4.00 atm of oxygen is mixed with 0.500 atm of hydrogen and no water is initially present. What is the concentration of hydrogen gas after equilibration.
b. Consider a system, also at 1000.0 K, where 0.250 atm of oxygen is mixed with 0.500 atm of hydrogen and 2.000 atm of water. What is the concentration of hydrogen and oxygen gas after equilibration.

Solution

a)

$$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(l)$$

$$K = 3.4 = \frac{1}{P_{H_2}^2 P_{O_2}}$$

$$P_{H_2} = 1.2\,\text{atm}$$

$$3.4 = \frac{1}{(1.2)^2 P_{O_2}}$$

$$P_{O_2} = \frac{1}{(1.2)^2(3.4)} = 0.204\,\text{atm}$$

b) Excess $H_2O(l)$ is added drive the reaction to the left towards the reactant to reach the equilibrium; therefore, pressure of H_2 and O_2 increased.

	$2\,H_2(g)$	$O_2(g)$	$2\,H_2O(l)$
Initial	0	0.3	N/A
Change	$+2x$	$+x$	N/A
Equilibrium	$2x$	$0.3+x$	N/A

$$K = \frac{1}{(2x)^2(0.3+x)} = 3.4$$

$$3.4(0.3+x)(2x)^2 = 1$$

$$x = 0.339\,\text{atm}$$

$$P_{O_2} = 0.3 + 0.339 = 0.639\,\text{atm}$$

$$P_{H_2} = 2(0.339) = 0.678\,\text{atm}$$

Q43

If you decompose ammonium nitrate into water and nitrous oxide, which further decomposes into oxygen and nitrogen gas, making the final reaction:

$$2\,NH_4NO_3(s) \rightleftharpoons 2\,N_2(g) + O_2(g) + 4\,H_2O(g)$$

This reaction takes place only in the molten salt, above its melting point of 169.6°C (for the anhydrous product). So, you get your 170°C blow torch and begin decomposing the ammonium nitrate under a sealed hood. Upon decomposition, all of the ammonium nitrate is gone, i.e. the reaction goes to completion.

a. What can be said of the equilibrium constant of this reaction at 170°C?
b. Now, in another universe, the partial pressure of $N_2(g)$ is 0.3 atm initially. Will the reaction still go to, essentially, completion?

Solution

(a) If there is no ammonium nitrate left, then the reaction was **heavily** products favoring, meaning K is extremely high at 170°C.

Note: It's more accurate to say that Q is a big number when there is no reactants left after reaction occurred. Reviewer's comment: Q stands for the current state. K is the equilibrium constant. When there is no reactant left after reaction occurred, the reaction is at the equilibrium state, so Q = K. Since Q is a big number, then K is also a big number.

(b) There would have to be an enormous amount of Nitrogen to force the reaction backwards. Because 0.3 atm is likely not enough to push back an essentially irreversible reaction, it has no noticeable affect on the amount of end product. (Note: If the reactants and products are essentially gas, we calculate the equilibrium constant not by its concentration, but by its pressure.)

Q45

Al_2Cl_6 at a partial pressure of 0.600 atm is placed in a closed container at 454 K. Al_3Cl_9 (partial pressure 1.98×10^{-3} atm) is also placed in it as well. Argon is added to raise the total pressure up to 1.00 atm.

Find whether if there is going to be net production or consumption of Al_3Cl_9 given $K_p = 1.04 \times 10^{-4}$. Then find the final pressure of Al_3Cl_9.

Solution

The reaction is

$$3\,Al_2Cl_6(g) \rightleftharpoons 2\,Al_3Cl_9(g)$$

Because argon does not react, it can be ignored.

$$Q = \frac{([Al_3Cl_9])^2}{([Al_2Cl_6])^3} = \frac{(1.98 \cdot 10^{-3})^2}{(0.600)^3} = 1.82 \cdot 10^{-5} < K_p = 1.04 \cdot 10^{-4}$$

There will be production of Al_3Cl_9.

ICE Table	Al_2Cl_6	Al_3Cl_9
Initial	0.600	1.98×10^{-3}
Change	$-3y$	$+2y$
Equilibrium	$0.6 - 3y$	$1.98 \times 10^{-3} + 2y$

$$K = 1.04 \cdot 10^{-4} \frac{([Al_3Cl_9])^2}{([Al_2Cl_6])^3} = \frac{(1.98 \times 10^{-3} + 2y)^2}{(1 - (1.98 \times 10^{-3} + 2y))^3}$$

Solving out

$$y = 0.0041 \text{ atm}$$

Al_3Cl_9 final pressure = 0.0102 atm.

Q46

The thermal decomposition of NH_4Cl solid proceeds as follows:

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

the equilibrium constant at 275°C is 1.04×10^{-2}. If the partial pressures of $NH_3(g)$ and $HCl(g)$ are equal, and the total partial pressure of the system is 0.200 atm, in what direction does the reaction proceed? What will be formed?

Solution

First, we make two equations to solve out the partial pressures. To get the first equation, we sum over the partial pressures to the total pressure. NH_4Cl is a solid, so it doesn't contribute to the partial pressure

$$P_{NH_3} + P_{HCl} = 0.200 \text{ atm}$$

The second equation is from the question that partial pressures of $NH_3(g)$ and $HCl(g)$ are equal

$$P_{NH_3} = P_{HCl}$$

Hence,

$$P_{NH_3} = P_{HCl} = 0.100 \text{ atm}$$

$$Q(\text{reaction quotient}) = P_{NH_3} P_{HCl} = (0.100)^2$$

$$10^{-2} < 1.04 \times 10^{-2}$$

$$Q < K$$

Hence, the reaction will slightly proceed more in the forward direction.

NH_3 and HCl will be formed.

Q47

A tube contains a mixture of NO_2 and N_2O_4 gas is set at 298K, in which the initial partial pressure NO_2 is 0.38 atm, and the initial partial pressure of N_2O_4 is 0.59 atm. NO_2 is a brownish gas, while N_2O_4 is a colorless gas.

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$$

a. What is the reaction quotient at the start of this reaction?
b. As the reaction shown above reaches equilibrium, the mixture becomes more brown. With this in mind, is the equilibrium constant, $K_{p,}$ greater than or less than the Q calculated in part a?

Solution

a)

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$$

$$P_{N_2O_4} = 0.59 \text{ atm} \quad P_{NO_2} = 0.38 \text{ atm}$$

$$Q_p = \frac{P_{N_2O_4}}{(P_{NO_2})^2}$$

$$Q_p = \frac{0.59}{0.38^2} = 4.1$$

b) Since the mixture becomes more brown as the reaction reaches equilibrium, more NO gas is being produced, therefore the reverse reaction is favored, so $Q_p > k_p$, in conclusion, $K_p < 4.1$.

Q49

At 500 K the equilibrium constant for the reaction:

$$\mathrm{PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)}$$

is $K_{eq} = 2.1$. Suppose the equilibrium is disturbed and shifts, while temperature remains constant. Calculate the reaction quotient for each one of the possible changes in equilibrium concentration given below and evaluate in what direction the reaction will shift to reestablish equilibrium.

a. $[PCl_3]$= 0.0563, [Cl2]= 0.0784, $[PCl_5]$= 0.8934.
b. $[PCl_3]$=0.4390 , [Cl2]= 0.3547, $[PCl_5]$= 0.1048.
c. $[PCl_3]$= 0.4018, [Cl2]= 0.8690, $[PCl_5]$= 0.7205.

Q48

NO_2 has a brownish color. At elevated temperatures, NO_2 reacts with CO

$$\mathrm{NO_2(g) + CO(g) \rightleftharpoons NO(g) + CO_2(g)}$$

The other gases in this equation are colorless. When a gas mixture is prepared at 600K, in which 9.6 atm is the initial partial pressure of both NO_2 and CO, and 5.4 atm is the partial pressure of both NO and CO_2, the brown color of the mixture observed begins to get stronger as the reaction progresses toward equilibrium. Give a condition that must be satisfied by the equilibrium constant K.

Q51

The equilibrium constant (K_p) for the reaction

$$\mathrm{As_4(g) \rightleftharpoons 2\,As_2(g)}$$

is 5.5837×10^{-4} at 1090 K.

a. The initial molarity of $[\mathrm{As_4}]$ is 2.3 M and the initial molarity of $[\mathrm{As_2}]$ is 0.001 M. Calculate the reaction quotient Q and determine which way the reaction proceeds.
b. Calculate the molarity of each compound at the equilibrium.
c. Which direction will the reaction proceed if the pressure on the reaction decreases? Explain your answer.

Solution

(a) First, because you are given the initial molarities of your products and reactants and a Kp instead of a Kc value, you have to convert Kp to Kc using the formula:

$$K_p = K_c(RT)^{\Delta n_{\text{gas}}}$$

Plug in your given values

$$5.5837 \times 10^{-4} = K_c(0.0821 \times 1090)^{2-1} = 89.489 K_c$$

$$K_c = 6.24 \times 10^{-6}$$

Set up a reaction quotient for the equation given

$$Q = \frac{[\mathrm{As_2}]^2}{[\mathrm{As_4}]} = \frac{[0.001]^2}{[2.3]} = 4.35 \times 10^{-7}$$

Reaction will progress towards the right to reach equilibrium

(b) Set up an ice chart to find the equilibrium molarities

Reaction	P_4	2 P_2
I	2.3	0.001
C	$-x$	$+2x$
E	$2.3-x$	$0.001+2x$

$$6.24\times10^{-6}=\frac{[0.001+2x]^2}{[2.3-x]}$$

$$4x^2+0.00400624x-1.3352\times10^{-5}=0$$

Use the quadratic equation to find x

$$x=-0.0024, 0.00139$$

-0.0024 is negative, which can't happen in real life so we know \(x) actually equals 0.00139.

$[P_4]$= 2.29861 M

$[P_2]$= 0.00378 M

(c) The reaction will progress towards the right because as pressure decreases, the reaction moves towards the side with the most moles of gas, which is the products.

Q55

Consider a reaction involving only gaseous compounds. The product yield at equilibrium decreases when the temperature and volume increase.

a. Is this reaction endothermic or exothermic?
b. Does the number of gas molecules in this reaction increase or decrease?

Solution

a. Exothermic. In exothermic reactions, product yield is indirectly related to temperature. In endothermic reactions, product yield is directly related to temperature. These properties can be further explained when heat is thought of as a reactant or a product. In exothermic reactions, heat is a product, and in endothermic reactions, heat is a reactant. When heat is added to a reaction, the equilibrium shifts to the opposite side to relieve stress on the system.

b. Decreases. The number of gas molecules is directly related to the volume of the container in which the reaction is happening. For example, if the volume of the container is decreased, the reaction will shift to whichever side has fewer moles of gas.

Q57

the Haber process, also called the Haber–Bosch process, is an artificial nitrogen fixation process and is the main industrial procedure for the production of ammonia today.

$$N_3+3\,H_2 \rightleftharpoons 2\,NH_3 \quad (\Delta H=-92.4\,kJ/mol)$$

Determine the best condition of temperature and pressure to yield the most ammonia.

Solution

Because Haber process is an exothermic reaction, a lower temperature will maximize the yield of product. Also, according to the ideal gas law, because the moles of gas are proportional to the volume, and the volume is inverse proportional to the pressure; a higher pressure is required to maximize the yield of product.

Q59

At room temperature, a vessel is filled with gaseous carbon dioxide. Some water is added at 2.00 atm. It is well-shaken, integrating carbon dioxide gas into the water. 0.5 kg of the solution is taken out and boiled to extract 2.50 L of carbon dioxide. The system is at 10 degree Celsius and 1.00 atm. What is the Henry's Law constant for carbon dioxide in water?

Solution

given that the extracted solution:

$$PV = nRT \tag{14.E.1}$$

$$n = \frac{PV}{RT} = \frac{1\,\text{atm} \times 2.5\,\text{L}}{0.082\,\frac{\text{L atm}}{\text{mol K}} \times 283.15\,\text{L}} = 0.1077\,\text{mol} \tag{14.E.2}$$

$$m_{\text{CO}_2} = n_{\text{CO}_2} \times \text{molar mass} = 0.1077\,\text{mol} \times 44\,\text{g/mol} = 4.7388\,\text{g} \tag{14.E.3}$$

$$m_{\text{H}_2\text{O}} = 500\,\text{g} - 4.7388\,\text{g} = 495.29\,\text{g} \tag{14.E.4}$$

$$n_{\text{H}_2\text{O}} = \frac{495.29\,\text{g}}{18\,\text{g/mol}} = 27.5\,\text{mol} \tag{14.E.5}$$

$$\text{Solubility of \textbackslash ce\{CO2\} in water} = \frac{0.1077\,\text{mol}}{0.5\,\text{kg}} = 0.2154\,\text{mol/kg} \tag{14.E.6}$$

Due to the Ideal gas law, the ratio of moles equals to the ratio of pressure

pressure: pressure = mol:mol = 0.1077: 27.51

because the total pressure is 2 atm, partial pressure of CO_2 = 0.0724 atm

Due to Henry's law:

$$k = \frac{c}{P} = \frac{0.2154 mol/kg}{0.0724\ atm} = 2.9751\,\frac{mol}{kg\,atm} \tag{14.E.7}$$

Q61

The equilibrium constant for a reaction increases from $K = 4 \cdot 5 \times 10^{-2}$ to $K = 4 \cdot 5$ as the temperature increases from 0.00°C to 300.0°C. Assuming the change in enthalpy (ΔH) and change in entropy (ΔS) are constant over this range of temperatures, what is ΔS for this reaction? Is this reaction endothermic or exothermic?

Solution

Assuming ΔH and ΔS are constant, we can set up a system of equations as follows:

$$\left\{ \begin{array}{l} \Delta G_{0.00^\circ\text{C}} = \Delta\text{H} - \text{T}\Delta\text{S} \\ \Delta G_{300.0^\circ\text{C}} = \Delta\text{H} - \text{T}\Delta\text{S} \end{array} \right.$$

We can determine $\Delta G_{0.00^\circ\text{C}}$ and $\Delta G_{300.0^\circ\text{C}}$ by utilizing the equation below that relates ΔG to K_{eq}:

$$\Delta G \;=\; -\text{RT}\ \ln(\text{K}) \quad \text{Easily remembered using the mnemonic: "}\Delta\text{Get in the }-\text{RighT lane, K?"}$$

$$\Delta G_{0.00^\circ\text{C}} \;=\; -\left(8.314\,\frac{\text{J}}{\text{K}\times\text{mol}}\right)(273.15\text{K})\left(\ln(4.5\times10^{-2})\right) \;=\; 7042.5\,\frac{\text{J}}{\text{mol}}$$

$$\Delta G_{300.0^\circ\text{C}} \;=\; -\left(8.314\,\frac{\text{J}}{\text{K}\times\text{mol}}\right)(573.15\text{K})\left(\ln(4.5)\right) \;=\; -7167.2\,\frac{\text{J}}{\text{mol}}$$

These values can then be plugged back into the original system of equations to obtain

$$\left\{ \begin{array}{l} \Delta G_{0.00^\circ\text{C}} = 7042.5\,\frac{\text{J}}{\text{mol}} = \Delta\text{H} - (273.15\text{K})\,\Delta\text{S} \\ \Delta G_{300.0^\circ\text{C}} = -7167.2\,\frac{\text{J}}{\text{mol}} = \Delta\text{H} - (573.15\text{K})\,\Delta\text{S} \end{array} \right.$$

To calculate the values of the remaining two unknown variables, a substitution can be made that expresses ΔH in terms of ΔS.

$$-7167.2\,\frac{\text{J}}{\text{mol}} + (573.15\text{K})\,\Delta\text{S} = \Delta\text{H}$$

This substitution can be plugged into the first equation to calculate the value for ΔS.

$$7042.5\frac{\text{J}}{\text{mol}} = -7167.2\frac{\text{J}}{\text{mol}} + (573.15\text{K})\,\Delta\text{S} - (273.15\text{K})\,\Delta\text{S}$$

$$\Delta\text{S} = 47.37\frac{\text{J}}{\text{K}\times\text{mol}}$$

ΔH can be calculated now by plugging in the value for ΔS into either one of the equations in the original set.

$$7042.5\frac{\text{J}}{\text{mol}} = \Delta\text{H} - (273.15\text{K})\left(47.37\frac{\text{J}}{\text{K}\times\text{mol}}\right)$$

$$\Delta\text{H} = 19980\frac{\text{J}}{\text{mol}} = 19.98\frac{\text{kJ}}{\text{mol}}$$

Because ΔH is positive, we know the reaction is endothermic.

Q63A

The equilibrium constant for the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\,\text{NO}_2(\text{g})$ is measured to be 5.9×10^{-3} at 298\;K and 1.3×10^{-6} at $398\ K$

a. Calculate ΔG° at 298 K for the reaction.
b. Calculate ΔH and ΔS°, assuming the enthalpy and entropy changes are independent of temperature between 298 K and 398 K.

Solution

a.Use the equation $\Delta G^\circ = -RT\ln K$

$\Delta G^\circ = -RT\ln K = (-8.3145\ \text{J K mol}^{-1})\times(298\ \text{K})(\ln 5.9\times10^{-3}) = -1.29\times10^{4}\ \text{J mol}^{-1}$

For one mole of the reaction as written, ΔG° is -1290 kJ.

b. Use van't Hoff equation and the values of K at 298 K and at 398 K to obtain ΔH°. Then get ΔS° from ΔG° and the equation $\Delta G^\circ = -RT\ln K$

$\ln(\frac{1.3\times10^{-6}}{5.9\times10^{-3}}) = \frac{\Delta H^\circ}{8.3145\ \text{J K}^{-1}\text{mol}^{-1}}(\frac{1}{398\ K} - \frac{1}{298\ K})$

$\Delta\ H^\circ = 83.0\ kJ$

The answer equals both $\Delta\ H^\circ$ at 298 K and 398 K because it is assumed in the derivation of the van't Hoff equation that $\Delta\ H^\circ$ is independent of temperature. Next,

$\Delta\ S^\circ = \frac{\Delta\ H^\circ - \Delta\ G^\circ}{T} = \frac{83.0\times10^{3}\ J - (-1.29\times10^{4}\ J)}{298\ K} = 323\ J\ K^{-1}$

Q63B

For the reaction: $\text{Br}_2(\text{g}) \rightleftharpoons 2\,\text{Br}(\text{g})$, the equilibrium constant is 4.64×10^{-29} at 25^{o}C and 1.1×10^{-3} at 1280 K.

a. What is ΔG of the reaction at 298 K?
b. Assuming that ΔH^o and ΔS^o are independent of temperature, what are the values of enthalpy and entropy when the temperature changes to 1280 K?

Solution

a. ΔG = RTln(k)

= (8.3145JK^{-1}mol^{-1})(298K)ln(4.64x10^{-29})

= -161.65kJ

a)

$$ln\left(\frac{1.1x10^{-3}}{4.64x10^{-29}}\right) = \frac{-\Delta H}{R}\left(\frac{1}{1280K} - \frac{1}{298K}\right)$$

Solve for Δ H.

Δ H = 188.70 KJ

$$ln\,(k) = \frac{-\Delta\,H}{RT} + \frac{\Delta S}{R}$$

ln \left({1.1x10^{-3}}\right) = \dfrac{-188699.30}{(8.3245;\ {JK^{-1}mol^{-1}})(1280:\K} + \dfrac{ ΔS}{R} \nonumber

ΔS $=90.78\ JK^{-1}mol^{-1}$

Q65

Calculate the equilibrium constant for the reaction,

$$2\ NO_2\ (g) \rightleftharpoons N_2O_4\ (g) \text{ at 500 K,}$$

given the equilibrium constant K = 4.65×10^{-3} at 298 K, and ΔH° = -57.2 kJ mol^{-1}. Assume that ΔH° does not change between 298 K and 500 K

Solution

Use the van 't Hoff equation to calculate K_{500} from K_{298} and the standard enthalpy of the reaction ΔH°:

$$ln\frac{K_{500}}{K_{298}} = -\frac{\Delta H^\circ}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$

=> $K_{500} = 3.366 \times 10^{-7}$

Solve for the unknown variable, in this case it is K_{500}. T_1 is equal to 298K while T_2 is equal to 500K.

Q69

The equilibrium constant for the following reaction was experientially calculated at different temperatures.

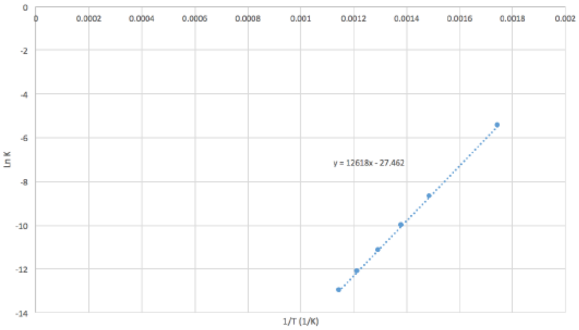
$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Temperature (°C)	300	400	450	500	550	600
Equilibrium Constant (K_{eq})	4.34×10^{-3}	1.64×10^{-4}	4.51×10^{-5}	1.45×10^{-5}	5.38×10^{-6}	2.25×10^{-6}

a. Plot $\ln K$ as a function of $1/T$ (K^{-1})
b. What is ΔH° of the equilibrium reaction with ammonia? HINT: use the slope to find the ΔH°

Solution

The graph bellow shows what the graph should look like:



First we must write the van't Hoff equation:

$$\ln K = -\frac{\Delta H^o}{R}\frac{1}{T} + \frac{\Delta S^o}{R}$$

Writing the equation like this how it can be compared with y = mx + b. With this information we then know that the slope of the graphe is equal to -ΔH^o/R. So:

$$\Delta H^o = \text{-mR were R} = 8.3145 \text{ J K}^{-1}\text{mol}^{-1}$$

$$\Delta H^o = -104.9 \text{ kJ mol}^{-1}$$

Q71

At a certain temperature, $0.5 \text{ mol } I_{2\ (aq)}$ is dissolved in $2 \text{ L } H_2O$ and shaken vigorously in a container with 2 L of CCl_4, an immiscible liquid. The container is then left to equilibrate during which time the iodine redistributes itself between the layers of H_2O and CCl_4 as indicated by the following reaction:

$$I_{2\ (aq)} \rightleftharpoons I_2(CCl_4)$$

The final concentration of $I_{2\ (aq)}$ is determined to be 0.0710 M. What is the partition coefficient (K) for this process?

Solution

The word "equilibrate" is a dead giveaway for "ICE Table" so we can establish the following ICE Table based on the information provided for the reaction provided.

$I_{2\ (aq)} \rightleftharpoons I_2(CCl_4)$

ICE Table	$I_{2\ (aq)}$	$I_2(CCl_4)$
Initial	$0.250M$	$0M$
Change	$-x$	$+x$
Equilibrium	$0.0710M$	$+x$

x can be calculated by solving the following equation:

$$0.250M - x = 0.0710M$$

$$x = 0.179M$$

This value can then be plugged into the ICE Table to obtain equilibrium values for $I_{2\ (aq)}$ and $I_2(CCl_4)$. (Remember that the two liquids are immiscible so the molarity isn't $0.125M$as $I_2(CCl_4)$ does not contribute to the initial molarity of the solution.)

ICE Table	$I_{2\ (aq)}$	$I_2(CCl_4)$
Initial	$0.250M$	$0M$
Change	$-0.179M$	$+0.179M$
Equilibrium	$0.0710M$	$+0.179M$

The equilibrium concentrations of $I_{2\ (aq)}$ and $I_2(CCl_4)$ can then be plugged into the equilibrium constant expression and solve for the partition coefficient.

$$K = \frac{0.179M}{0.0710M}$$

$$K = 2.52$$

Q73

At 25°C, 0.130 g/L of chloroacetic acid ($C_2H_3ClO_2$) dissolve in of water, and at the same temperature 0.2834 g/L of chloroacetic acid dissolve in 1-octanol.

a. Calculate the following equilibrium constants

$$\mathrm{C_2H_2ClO_2H(s)} \rightleftharpoons \mathrm{C_2H_2ClO_2H}_{(aq)}$$

$$\mathrm{C_2H_2ClO_2H(s)} \rightleftharpoons \mathrm{C_2H_2ClO_2H}_{(octanol)}$$

b. Calculate the *participation coefficient*, K, of the combined reactions.

$$\mathrm{C_2H_2ClO_2H(aq)} \rightleftharpoons \mathrm{C_2H_2ClO_2H}_{(octanol)}$$

Solution

First, we will need g/L to M so that we can calculate the equilibrium constant.

$$\left(\frac{0.130\ \ g\,\cancel{C_2H_3ClO_2}}{1\ L}\right)\left(\frac{1\ mol}{94.494\ \ g\,\cancel{C_2H_3ClO_2}}\right) = 0.0013757\ M$$

$$\left(\frac{0.2834\ \ g\,\cancel{C_2H_3ClO_2}}{1\ L}\right)\left(\frac{1\ mol}{94.494\ \ g\,\cancel{C_2H_3ClO_2}}\right) = 3.00x10^{-3}\ M$$

$$K = \frac{K_{forminde}}{K_{aq}} = \frac{3.00\times10^{-3}}{0.001376} = 2.18$$

$$\log_{10} K_{oct/wat} = 0.338$$

Q75

At 298 K, the two gases NOBr and Br_2 have the number of moles of 1.25 and 8.5 x 10^{-5} at equilibrium with a sufficient amount of solid NO. Determine the equilibrium constant of the reaction:

$$2NOBr_{(g)} \rightleftharpoons 2NO_{(s)} + Br_{2(g)}$$

Solution

Use: $P_{gas} = n_{gas}(RT/V)$

$K = P_{Br2} / P^2_{NOBr} = n_{Br2} / n^2_{NOBr} = 5.44 \times 10^{-5}$

The volume is needed to solve this problem. It is necessary to find the value of K regardless of it is K_p or K_c.

Q79

At 300 K and 1 atm, N_2O_4 is partly dissociated into NO_2. The density of the equilibrium mixture was 2.076 g/L. What is the degree of dissociation of N_2O_4 under these circumstances?

Solution

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

moles of N_2O_4 at equilibrium = 1-x moles of NO_2 at equilibrium = 2x

Therefore, the degree of dissociation of SO_3 is 0.8.

(Multiplying number of moles by molar mass to get the total mass)

92*(1- x) + [46*(2x)/ (1+x)]= [2.076 g/L * 0.08206 (L*atm)/(mol*K)] / 1 atm

On solving the equation, we get the equation, x= 0.8

Q85

The decompressions of calcium carbonate ($\mathrm{CaCO_3}$) occurs according to the following reaction:

$$\mathrm{CaCO_3(s)} \rightleftharpoons \mathrm{CaO(s)} + \mathrm{CO_2(g)}$$

100 g of solid calcium carbonate ($\mathrm{CaCO_3}$) and 50 g of calcium oxide (CaO) are placed in an evacuated round bottom flask that is heated up to 35°C. At this temperature the pressure in the round bottom flask is found to be 0.5 atm.

a. What is the equilibrium constant of the decompressions of calcium carbonate ($\mathrm{CaCO_3}$) at 35°C?
b. If 100 g of calcium oxide (CaO) at 35°C was added to the flask what would be the new total pressure of the flask and why?
c. If the pressure in the round bottom flask would to increase to 1.0 atm, then what would would be the new equilibrium constant?

Solution

a. First we need to write the equilibrium expression for the reaction:

$$K_{eq} = p\mathrm{CO_2}] \tag{14.E.8}$$

Now we just need to plug in the pressure of CO_2: K_{eq} = [0.5] = 0.5

b. The total pressure would still be 0.5 atm because solids have an activity of 1 so they don't effect the equilibrium pressure.
c. The new equilibrium constant would be 1.0 atm.

Q87

Let's say you have the reaction:

$$A(s) + B(g) \leftrightharpoons C(s) + D(g)$$

At 25°C, this reaction has an equilibrium constant of 157.2. Find the partial pressures of $B(g)$ and $D(g)$ when the total pressure of the system is equal to 4.3 atm.

Solution

First, the equilibrium expression of this reaction is

$$K_c = \frac{D(g)}{B(g)} = 157.2$$

Note, the A(s) and C(s) are not included in this expression because they are solids. Solids have an activity equal to 1 which basically means they do not affect the equilibrium of the reaction.

To calculate the partial pressure of our unknowns, we can use Dalton's Law of partial pressures:

$$P_A = X_A P_{Total}$$

Since we are looking for the partial pressure of each of our gases, and we already have the total pressure of the system, we need to find the mole fraction of each of our gases. To find it, we can manipulate the above equilibrium expression to get:

$$D(g) = 157.2\ B(g)$$

Here, we see that at equilibrium, there are 157.2 molecules of $D(g)$ for every 1 molecule of $B(g)$

Now that we have the ratio of molecules in this reaction, we can construct workable mole fractions.

$$X_D = \frac{157.2}{1+157.2}$$

$$X_B = \frac{1}{1+157.2}$$

Finally, we can plug everything in to find our partial pressures.

$$P_D = \frac{157.2}{158.2} \times (4.3\ atm) = 4.27\ atm$$

$$P_B = \frac{1}{157.8} \times (4.3\ atm) = 0.027\ atm$$

Q91

Given the reaction

$$C_3H_5N(g) + 3\ H_2(g) \leftrightharpoons C_5H_{11}N(g)$$

whose equilibrium constant is solved by this equation

$$log_{10}(K) = -20.28 + \frac{10.56\ K}{T}$$

a. Solve for K when $T = 200\ K$
b. What is partial pressure of $C_3H_5N(g)$ when $T = 200\ K$ and the partial pressure of hydrogen is 1.0 atm and the partial pressure of $C_5H_{11}N(g)$ is 2.0×10^{-5} atm.

Solution

Part a)

$$log_{10}(K) = -20.28 + \frac{10.56\ K}{200\ K}$$

$$K = 10^{-20.23} = 5.89 \times 10^{-21}$$

part b)

Set up the equilibrium constant of the reaction, plug in your partial pressures, and solve for $C_3H_5N(g)$

$$K = \frac{[C_5H_{11}N]}{[C_5H_5N]\ [H_2]^3}$$

$$K = \frac{2.0 \times 10^{-5}}{[C_5H_5N]\ [1]}$$

$$[C_5H_5N] = 3.40 \times 10^{15}$$

Q93

Two equal volume solutions of 2M $HCOO^-$ and 2M HCOOH are mixed together. Assume that the volumes are additive. The value of the equilibrium constant Ka for HCOOH is 1.77 x 10^{-4}. What is the ratio between the amounts of HCOOH and $HCOO^-$ in the solution at equilibrium?

Solution

The chemical equation for this reaction is

$$HCOOH_{(aq)} + H_2O_l \leftrightarrow H_3O^+_{(aq)} + HCOO^-_{(aq)}$$

This indicates that

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

Because the volumes are equal and additive, the concentrations of the two solutions become half of what they were initially.

At equilibrium,

$$[HCOO^-] = 1 + x$$

$$[H_3O^+] = x$$

$$[HCOOH] = 1 - x$$

Plugging in these values into the equilibrium expression gives

$$1.77 \bullet 10^{-4} = \frac{[1+x][x]}{[1-x]}$$

Solving the equation for x gives

$$x = 1.77 \bullet 10^{-4} M$$

The ratio of HCOOH and $HCOO^-$ is

$$\frac{1+x}{1-x}$$

and due to x being such a small value, the ratio between the amounts of HCOOH and HCOO- is essentially 1.

Q101

The \(ΔG_f^o\) of $\mathrm{PbO(s)}$ is -188.95 kJ mol^{-1}. Calculate the equilibrium pressure of O_2(g) over a sample of pure PbO(s) in contact with pure Pb(s) at 25°C. PbO(s) decomposes according to the equation

$$\mathrm{PbO}_{(s)} \rightleftharpoons \mathrm{Pb(s)} + \tfrac{1}{2}\mathrm{O_2(g)}$$

Solution

Since G_f° for O_2(g) and Pb_s(s) is 0, for the reaction

$$\Delta G^\circ = (0+0) - (-188.95 kJmol^{-1}) = 188.95 kJmol^{-1}$$

The equilibrium constant of the reaction can be computed by

$$lnK = -\frac{\Delta G^\circ}{RT} = -76.22$$

$$K = 7.898 \bullet 10^{-34}$$

From the chemical equation, we can tell

$$K = (P_{O_2})^{1/2}$$

Therefore the equilibrium pressure of O_2 at 25°C

$$P_{O_2} = 6.2 \bullet 10^{-67} atm$$

Q105

If that weren't enough, Jim's sister, ., knocked his grass juice (a mixture of 1-Hexanol, Cl_2, $CaCl_2$, and cyclohexane) into the family's benzene-ethanol vat! Assume that the two solvents in the vat are immiscible with each other but are miscible with the grass juice components. Jim separates the benzene and ethanol, and drinks the one with the greater amount of 1-Hexanol. Which one does he drink? Which of the two solvents have the highest concentration of the other components of the grass juice?

Solution

There are two immiscible solvents in the family vat. What this means is that they do not mix/ dissolve well in each other. Consequently, when . poured the grass juice into this vat, the solution technically contains two solvents. Evidently, what this means is that each of the solutes (which are the grass juice constituents mentioned in the question) dissolves to a different extent in each solvent. When the question asks which solvent has the greater amount of 1-Hexanol, it is the same as asking does 1-Hexanol dissolve "more" in either benzene or ethanol (the two solvents). The concept of "like dissolves like" is very important here, and to solve this problem first benzene must be identified as non-polar and driven by dispersion forces, while ethanol is polar. Since polar solvents dissolve polar solutes, then ethanol should be able to dissolve $CaCl_2$ and 1-Hexanol, both polar solutes, much better, while benzene can dissolve Cl_2 and cyclohexane, which are nonpolar, to a greater extent. The aptitude that each solvent has in dissolving the solutes directly correlate to the concentrations of solutes that are present in the solvent.

Thus, Jim would drink the ethanol, since it has the highest concentration of the polar 1-Hexanol. Also, the benzene would have the highest concentration of Cl_2 and cyclohexane, and the ethanol would also have the highest concentration of $CaCl_2$, which is ionic and therefore "very polar".

Abstract: "Like dissolves Like": polar solvents dissolve polar solutes, and nonpolar solvents dissolve polar solutes

Q107

Calculate the pH of a 0.5 M H_3PO_4 acid solution given that $K_{a1} = 7.1 \times 10^{-3}$, $K_{a2} = 6.3 \times 10^{-8}$ and $K_{a3} = 4.2 \times 10^{-13}$.

Solution

A14.107V2

1.25

H14.107V2

Review on how to calculate the pH of a polyprotic acids here.

S14.107V2

$$7.1\times 10^{-3}=\frac{x^2}{(0.5-x)}$$

$$x=0.0561\ M=[H^+]$$

$$pH=-\log[H^+]=1.25$$

We assume that all of the H^+ in solution comes from the dissociation of the first H^+ because the second and the third is too small to have a significant effect in the pH of the solution.

Q107

The Haber-Bosch process is a method invented in the 20th century as a method for hydrogen fixation. It is widely used in industry today, and involves reacting nitrogen and hydrogen in the following manner:

$$N_2(g)+3\,H_2(g)\rightleftharpoons 2\,NH_3(g)$$

Calculate ΔG°_{rxn}. If the pressure of the products and reaction are all kept constant at the same value, in which direction will the reaction go?

Relevant information:

$$\Delta G^\circ_f\ NH_{2\,(g)}=199.83\frac{kJ}{mol}$$

Solution

The process of calculating ΔG should be very familiar after reading Q15, so this solution will not elaborate much on this method. With that being said, the ΔG°_{rxn} is as follows:

$$\Delta G^\circ_{rxn}=399.66\frac{kJ}{mol}$$

Both N_2 and H_2 have respective ΔG_f of zero. Now, remember that if ΔG°_{rxn} is negative (ΔG°_{rxn}<0), then the reaction is spontaneous in the direction mentioned. However, in this case the ΔG°_{rxn} is definitely NOT less than zero, so it is not spontaneous in the direction $N_{2\,(g)}+3H_{2\,(g)}\rightarrow 2NH_{3\,(g)}$. However, if the chemical formula is "flipped" so that it goes from $N_{2\,(g)}+3H_{2\,(g)}\leftarrow 2NH_{3\,(g)}$, Hess's law states that the corresponding ΔG°_{rxn} is also "flipped" from positive to negative (or vice versa, depending on the value. For this situation, however, the ΔG°_{rxn} does turn negative). What information can be drawn from this is that, since a negative ΔG°_{rxn} means that the reaction will be spontaneous, then it can be inferred that the reaction will favor going from $N_{2\,(g)}+3H_{2\,(g)}\leftarrow 2NH_{3\,(g)}$, rather than $N_{2\,(g)}+3H_{2\,(g)}\rightarrow 2NH_{3\,(g)}$. Without even having to calculate the equilibrium constant, from this information alone, it can be inferred that, at equilibrium, the reactants are favored over the products. Therefore, if both gasses are kept at constant pressure, the reaction will tend to increase concentration of reactants. Thus, the reaction will go left.

Abstract: Find the ΔG°_{rxn}, understand what implications it has in regards to equilibrium, and apply this knowledge to infer that the reaction will favor the reactants.

Q109

At 273 K, the equation: $H_2(g) + I_2(g) \rightarrow 2HI(g)$ has an equilibrium constant of 60.2

a. Solve for ΔG° at 273 K
b. How does G change when the pressure of HI is 2 atm, I_2 is 4 atm and H_2 is 6 atm?
c. Is this reaction spontaneous?

Solution

a) ΔG° = -RT ln(K)

ΔG° = -(8.3145 J/K mol)(273 K) ln(60.2)

ΔG° = -9301.1 J/mol

b) ΔG = ΔG° + RT ln(Q)

ΔG = -9301.1 J/mol + (8.3145 J/K mol)(273 K) ln(P_{HI} / $P_{H2}P_{I2}$)

ΔG = -9301.1 J/mol + (8.3145 J/K mol)(273 K) ln(2 / (6x4))

ΔG = -14941.49 J/mol.

c) This reaction proceeds spontaneously in the forward direction.

Q109

At 773 K the equilibrium constant for the Haber-Bosch process is 1.45x10^{-5}. The chemical reaction involved in the Haber-Bosch process is:

$$N_{2\ (g)} + 3H_{2\ (g)} \rightleftharpoons 2NH_{3\ (g)}$$

a. What is $\Delta G^\circ(773)$ for this reaction?
b. What is ΔG at 773 K for transforming 1 mole of N_2 and 3 moles H_2 held at 30 atm to 2 moles of NH_3 held at 1 atm?
c. In which direction would the previous reaction run spontaneously?

Solution

a. The value of $\Delta G^\circ(773)$ can be found using the equation $\Delta G^\circ = -RT\ln K$ where T and K are already known to be 773 K and 1.45x10^{-5} respectively while R=8.134 J K^{-1} mol^{-1}.

$$\Delta G^\circ = -8.314\ J\ K^{-1}\ mol^{-1} \times 773K \times ln(1.45 \times 10^{-5}) = 70052\ J$$

$$\Delta G^\circ = 70052\ J$$

b. The equation needed to determine ΔG is $\Delta G = RTln(Q/K)$. The values of R, T, and K are known while Q is

$$Q = \frac{P^2_{NH_3}/P_{ref}}{(P_{N_2}/P_{ref})(P^3_{H_2}/P_{ref})}$$

P_{ref} =1 atm and the other pressures are stated in the question. So to find Q, the pressures have to be plugged into the equation

$$Q = \frac{(1)^2}{(20)(20)^3} = \frac{1}{160000} = 6.25 \times 10^{-6}$$

Now that the value of Q is known, ΔG can be found

$$\Delta G = -8.314\ J\ K^{-1}\ mol^{-1} \times 773K \times ln(\frac{6.25 \times 10^{-6}}{1.45 \times 10^{-5}}) = -5291\ J$$

$$\Delta G = -5291\ J$$

c. The previous reaction would run towards the products spontaneously because $\Delta G < 0$.

Q111

The following reaction is exothermic

$$\mathrm{SnO_2(s) + 2\,H_2(g) \rightarrow Sn(g) + 2\,H_2O(l)}$$

a. What is the equilibrium expression based on this chemical equation?
b. What happens to the reaction if more H_2 is added? SnO_2 is added into the system?
c. What effect would an increase in temperature have on the system?
d. What affect would an increase in pressure have on the system?

Solution

a. Add texts here. Do not delete this text first.K = [Sn] / [H_2] This is because solids are not included in the equilibrium expression
b. If H_2 were added, the reaction would shift right, towards the products, more Sn is produced. If SnO_2 were added, there would be no effect on the equilibrium because SnO_2 is not involve in the equilibrium process (K).
c. The reaction would shift towards the reactants. The reaction is exothermic, so heat is treated like a product.
d. An increase in pressure would shift the reaction towards the side that has less mole of gas. Therefore, in this reaction, an increased in pressure would shift the reaction to the right, more products are produced. Q111

Q112

Given the chemical reaction

$$\mathrm{SnO_2(s) \rightleftharpoons Sn(s) + O_2(g)}$$

a. Formulate the equilibrium expression using activities
b. State the effect on $p\mathrm{O_2}$ at equilibrium if more $\mathrm{SnCl_4(l)}$ is added to the system
c. State the effect on $p\mathrm{O_2}$ at equilibrium if more $\mathrm{O_2(g)}$ is added to the system

Solution

a. The activities of solids and liquids are always equal to 1. The activities of gases are equal to the partial pressure of the gas in bars. Therefore the equilibrium expression would be

$$K = P_{O_2}$$

b. P_{O_2} would not change because the activity of a liquid is always 1 meaning it has no effect on the equilibrium constant

c. P_{O_2} would decrease because the extra gas would push the system out of equilibrium and in order for the system to return to equilibrium, some of the O_2 gas would have to react with some of the $Sn_{(s)}$. This would decrease the amount of $O_{2(g)}$ present in the system and therefore decrease the the pressure of $O_{2(g)}$.

Q113

Arrange the following solutions in order of most acidic to basic: NaOH, NaCN, H_2SO_4, NH_4NO_3, NaCl

Solution

$$\mathrm{H_2SO_4 > NH_4NO_3 > NaCl > NaCN > NaOH} \tag{14.E.9}$$

Review acids bases here.

- H_2SO_4 is a strong acid.
- NH_4NO_3 is formed by a weak base (NH_4OH) and a strong acid (HNO_3). Hence, NH_4NO_3 is acidic.
- NaCl is formed by a strong base (NaOH) and a strong acid (HCl). Hence, it is a neutral salt.
- NaCN is formed by a strong base (NaOH) and a weak acid (HCN). Hence, NaCN is basic.
- NaOH is a strong base.

Q115

Given that the K_b values for $\mathrm{NH_3}$ and $\mathrm{NH_2NH_2}$ are 1.8×10^{-5} and 8.5×10^{-7}, respectively. Which is the stronger acid?

Solution

$$\mathrm{NH_2NH_2}$$

Calculate the K_a values first. Review on how to identify the strength of an acid from its K_a value here.

For NH_3,

$$K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

For NH_2NH_2,

$$K_a = \frac{(1.0 \times 10^{-14}}{8.5 \times 10^{-7}} = 1.18 \times 10^{-8}$$

Since the Ka value of NH_2NH_2 is larger, NH_2NH_2 is the stronger acid.

Q119

Calculate the pH of the following solutions.

a. 0.5 M $\text{NaCN}\,(K_a \text{ of HCN} = 6.2 \times 10^{-10})$
b. 0.01 M $\text{NH}_4\text{Cl}\,(K_b \text{ of NH}_3 = 1.8 \times 10^{-5})$

Solution

11.5 5.63

Ka=(1*10^{-14})/(1.8*10^{-5})=5.56*10^{-10}
5.56*10^{-10}=x^2/(0.01-x)
x=2.36*10^{-6}
pH= -log(x)= 5.63

H14.119V2

Review on the properties of salts here.

\[\ce{CN$^-$ (aq) + H$_2$O (l) <=> HCN (aq) + OH$^-$ (aq)}\]

Kb=(1*10^{-14})/(6.2*10^{-10})=1.62*10^{-5}

$$1.62 \times 10^{-5} = \frac{x^2}{0.5 - x} \tag{14.E.10}$$

x=0.00283

pOH= -log(x)= 2.55

pH= 14-pOH= 11.5

$$\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \tag{14.E.11}$$

Q131

Identify the stronger acid in each of the following combination. Explain.

a. HF and HBr
b. H_2SO_4 and H_2SO_3
c. HOCl and HOBr

Solution

14.131V2

HBr H_2SO_4 HOCl

Study the effect of structure on acids and bases.

S14.131V2

1. HBr is the stronger acid because Br less electronegative and therefore less polar as compared to HF.
2. H_2SO_4 is the stronger acid because as the number of attached oxygen on the O-H bonds increases, the less polar the molecule is.
3. For oxyacids, the less polar oxyacids are the ones that are more electronegative. Since Cl is more electronegative than Br, HOCl is the stronger acid.

Q137

Identify the Lewis acid and Lewis base for each of the following reaction.

a. $H^+(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq)$
b. $Al^{3+}(aq) + 6\,H_2O(l) \rightleftharpoons Al(H_2O)_6^{3+}(aq)$
c. $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

Solution

	Lewis acid	Lewis base
1.	H^+	NH_3
2.	Al^{3+}	H_2O
3.	CO_2	H_2O

H14.137V2

Study the concept of electron pairs here.

S14.137V2

H^+ is the electron-pair acceptor while NH_3 is the electron-pair donor. Al^{3+} is the electron-pair acceptor while H_2O is the electron-pair donor. CO_2 is the electron-pair acceptor while H_2O is the electron-pair donor.

Q139

Beryllium hydroxide is an amphoteric compound. It can react as an acid as well as a base. Please write the reactions of $Be(OH)_2$ and describe its role base on Brønsted-Lowry and Lewis theories.

Solution

$Be(OH)_2(s)+2H^+(aq)\text{->} Be^{2+}(aq)+2H_2O(l)$ (Brønsted-Lowry base, $2H^+$ acceptor)

$Be(OH)_2(s)+2OH^-(aq)\text{->} Be(OH)_4^{2-}(aq)$ (Lewis acid, electron pair acceptor)

H14.139.2P

Consider Brønsted-Lowry and Lewis theories.

http://chemwiki.ucdavis.edu/Textbook...cids_and_Bases

CHAPTER OVERVIEW

15: Acid–Base Equilibria

An General Chemistry Libretexts Textmap organized around the textbook
Principles of Modern Chemistry
by Oxtoby, Gillis, and Campion

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI
XVII XVIII XIX XX XXI XXII XXIII • **Homework Exercises**

Template:HideTOC

Acids and bases have been defined differently by three sets of theories. One is the Arrhenius definition, which revolves around the idea that acids are substances that ionize (break off) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide (OH^-) ions in solution. On the other hand, the Bronsted-Lowry definition defines acids as substances that donate protons (H^+) whereas bases are substances that accept protons. Also, the Lewis theory of acids and bases states that acids are electron pair acceptors while bases are electron pair donors. Acids and bases can be defined by their physical and chemical observations.

15.1: Classifications of Acids and Bases

Learning Objectives

- To understand the differences between the three definitions of Acids and Bases
- Identify acids, bases, and conjugate acid-base pairs according to the three definitions of Acids and Bases
- To understand the concept of conjugate acid–base pairs in acid/base reactions
- Write the equation for the proton transfer reaction involving a Brønsted-Lowry acid or base, and show how it can be interpreted as an **electron-pair transfer** reaction, clearly identifying the donor and acceptor.
- Give an example of a **Lewis acid-base reaction** that does not involve protons.

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Carl Axel Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Acids and bases are common solutions that exist everywhere. Almost every liquid that we encounter in our daily lives consists of acidic and basic properties, with the exception of water. They have completely different properties and are able to neutralize to form H_2O, which will be discussed later in a subsection. Acids and bases can be defined by their physical and chemical observations (Table $15.1.1$).

Table 15.1.1: General Properties of Acids and Bases

ACIDS	BASES
produce a piercing pain in a wound.	give a slippery feel.
taste sour.	taste bitter.
are colorless when placed in phenolphthalein (an indicator).	are pink when placed in phenolphthalein (an indicator).
are red on blue litmus paper (a pH indicator).	are blue on red litmus paper (a pH indicator).
have a pH<7.	have a pH>7.
produce hydrogen gas when reacted with metals.	
produce carbon dioxide when reacted with carbonates.	
Common examples: Lemons, oranges, vinegar, urine, sulfuric acid, hydrochloric acid	Common Examples: Soap, toothpaste, bleach, cleaning agents, limewater, ammonia water, sodium hydroxide.

Acids and bases in aqueous solutions will conduct electricity because they contain dissolved ions. Therefore, acids and bases are *electrolytes*. Strong acids and bases will be strong **electrolytes**. Weak acids and bases will be weak electrolytes. This affects the amount of conductivity.

In chemistry, acids and bases have been defined differently by **three sets of theories**: One is the Arrhenius definition defined above, which revolves around the idea that acids are substances that ionize (break off) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide (OH^-) ions in solution. The other two definitions are discussed in detail include the **Brønsted-Lowry definition** the defines acids as substances that donate protons (H^+) whereas bases are substances that accept protons and the **Lewis theory** of acids and bases states that acids are electron pair acceptors while bases are electron pair donors.

Arrhenius Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. The Arrhenius definition of acid-base reactions is a development of the "hydrogen theory of acids". It was used to provide a modern definition of acids and bases, and followed from Arrhenius's work with Friedrich Wilhelm Ostwald in establishing the presence of ions in aqueous solution in 1884. This led to Arrhenius receiving the Nobel Prize in Chemistry in 1903.

An **Arrhenius acid** is a compound that increases the concentration of H^+ ions that are present when added to water.

$$\mathrm{HCl(g) \rightarrow H^+(aq) + Cl^-(aq)} \tag{15.1.1}$$

In this reaction, hydrochloric acid (HCl) gas dissociates into hydrogen (H^+) and chloride (Cl^-) ions when dissolved in water, thereby releasing H^+ ions into solution. These H^+ ions form the hydronium ion (H_3O^+) when they combine with water molecules. Both processes can be represented in a chemical equation by adding H_2O to the reactants side of Equation 15.1.1 and switching hydronium ions for free protons.

$$\mathrm{HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)} \tag{15.1.2}$$

An **Arrhenius base** is a compound that dissociates to yield hydroxide ions (OH^-) in aqueous solution. Common examples of Arrhenus bases include Sodium hydroxide ($NaOH$), Potassium hydroxide (KOH), Magnesium hydroxide $Mg(OH)_2$, and Calcium hydroxide ($Ca(OH)_2$. All of these bases are solids at room temperature and when dissolved in water, will generate a metal cation and the hydroxide ion ((OH^-), for example, Sodium hydroxide

$$\mathrm{NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)} \tag{15.1.3}$$

All Arrhenius acids have easily detachable hydrogen that leave to form hydronium ions in solution and all Arrhenius bases have easily detachable OH groups that form hydroxide ions in solution.

Limitation of the Arrhenius Definition of Acids and Bases

The Arrhenius definitions of acidity and alkalinity are restricted to aqueous solutions and refer to the concentration of the solvated ions. Under this definition, pure H_2SO_4 or HCl dissolved in toluene are not acidic, despite the fact that both of these acids will donate a proton to toluene. In addition, under the Arrhenius definition, a solution of sodium amide ($NaNH_2$) in liquid ammonia is not alkaline, despite the fact that the amide ion (NH_2^-) will readily deprotonate ammonia. Thus, the Arrhenius definition can only describe acids and bases in an aqueous environment. The Arrhenius definition can **only** describe acids and bases in protic solvents and environments (e.g., water, alcohols, within proteins etc.).

Brønsted-Lowry Acids and Bases

The Arrhenius definitions identified an acid as a compound that dissolves in water to yield hydronium ions (Equation 15.1.2) and a base as a compound that dissolves in water to yield hydroxide ions (Equation 15.1.3). As mentioned above, this definition limited. We extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H^+. A proton is what remains when a normal hydrogen atom, ${}^1_1H$, loses an electron. A compound that donates a proton to another compound is called a **Brønsted-Lowry acid**, and a compound that accepts a proton is called a **Brønsted-Lowry base**. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base).

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O. Anions (such as HSO_4^-, $H_2PO_4^-$, HS^-, and HCO_3^-) and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_6]^{3+}$) may also act as acids.

Bases fall into the same three categories and may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as $NaOH$ and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$\mathrm{H^+ + OH^- \rightarrow H_2O} \tag{15.1.4}$$

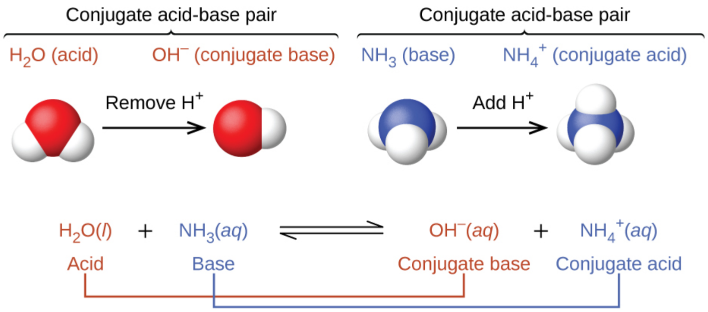
We call the product that remains after an acid donates a proton the **conjugate base** of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\begin{aligned}\text{acid} &\rightleftharpoons \text{proton} + \text{conjugate base}\\ HF &\rightleftharpoons H^+ + F^-\\ H_2SO_4 &\rightleftharpoons H^+ + HSO_4^-\\ H_2O &\rightleftharpoons H^+ + OH^-\\ HSO_4^- &\rightleftharpoons H^+ + SO_4^{2-}\\ NH_4^+ &\rightleftharpoons H^+ + NH_3\end{aligned}$$

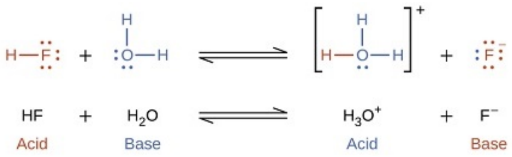
We call the product that results when a base accepts a proton the base’s **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base):

$$\begin{aligned}\text{base} + \text{proton} &\rightleftharpoons \text{conjugate acid}\\ OH^- + H^+ &\rightleftharpoons H_2O\\ H_2O + H^+ &\rightleftharpoons H_3O^+\\ NH_3 + H^+ &\rightleftharpoons NH_4^+\\ S^{2-} + H^+ &\rightleftharpoons HS^-\\ CO_3^{2-} + H^+ &\rightleftharpoons HCO_3^-\\ F^- + H^+ &\rightleftharpoons HF\end{aligned}$$

In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:



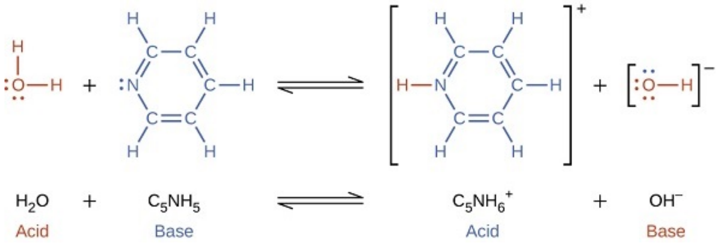
The reaction between a Brønsted-Lowry acid and water is called acid ionization. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



with

$$K = \frac{[H_3O^+][F^-]}{[HF]}$$

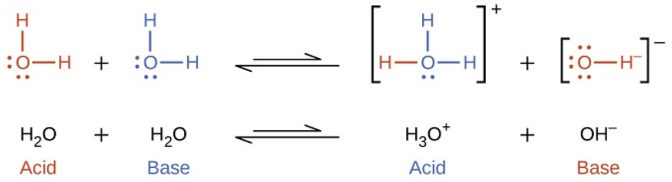
When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding ammonia to water yields hydroxide ions and ammonium ions:



with

$$K=\frac{[C_5NH_6^+][OH^-]}{[C_5NH_5]}$$

Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$H_2O(l)+H_2O(l)\rightleftharpoons H_3O^+(aq)+OH^-(aq) \tag{15.1.5}$$

with

$$K_\text{w}=[H_3O^+][OH^-] \tag{15.1.6}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is approximately 5.1×10^{-13}, roughly 100-times larger than the value at 25 °C.

✓ Example 15.1.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+]=[OH^-]$. At 25 °C:

$$\begin{aligned}K_\text{w}&=[H_3O^+][OH^-]\\&=[H_3O^+]^2\\&=[OH^-]^2\\&=1.0\times 10^{-14}\end{aligned}$$

So

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

? Exercise 15.1.1

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. Example $15.1.2$ demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

✓ Example 15.1.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

The Inverse Proportionality of [H_3O^+] and [OH^-] A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of [H_3O^+]:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Chatelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

? Exercise 15.1.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M$$

Amphoteric Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic. Another term used to describe such species is amphoteric, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$HCO{-}3\,(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

✓ Example 15.1.3: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of HSO_3^-

a. as an acid with OH^-
b. as a base with HI

Solution

a. $HSO_3^-(aq) + OH^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H_2O_{(l)}$
b. $HSO_3^-(aq) + HI(aq) \rightleftharpoons H_2SO_3(aq) + I^-(aq)$

? Exercise 15.1.3

Write separate equations representing the reaction of $H_2PO_4^-$

a. as a base with HBr
b. as an acid with OH^-

Answer a

$$H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)$$

Answer b

$$H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O_{(l)}$$

Lewis Acids and Bases

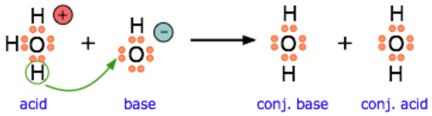
The Brønsted-Lowry proton donor-acceptor concept has been one of the most successful theories of Chemistry. But as with any such theory, it is fair to ask if this is not just a special case of a more general theory that could encompass an even broader range of chemical science. In 1916, G.N. Lewis of the University of California proposed that the *electron pair* is the dominant actor in acid-base chemistry. The Lewis theory did not become very well known until about 1923 (the same year that Brønsted and Lowry published their work), but since then it has been recognized as a very powerful tool for describing chemical reactions of widely different kinds and is widely used in organic and inorganic chemistry. The Brønsted–Lowry concept of acids and bases defines a base as any species that can accept a proton, and an acid as any substance that can donate a proton. Lewis proposed an alternative definition that focuses on *pairs of electrons* instead. According to Lewis:

- An *acid* is a substance that **accepts** a pair of electrons, and in doing so, forms a covalent bond with the entity that supplies the electrons.
- A *base* is a substance that **donates** an unshared pair of electrons to a recipient species with which the electrons can be shared.

> *In modern chemistry, electron donors are often referred to as nucleophiles, while acceptors are electrophiles.*

Lewis Acid-Base Neutralization Involving Electron-Pair Transfer

Just as any Arrhenius acid is also a Brønsted acid, any Brønsted acid is also a Lewis acid, so the various acid-base concepts are all "upward compatible". Although we do not really need to think about electron-pair transfers when we deal with ordinary aqueous-solution acid-base reactions, it is important to understand that it is the opportunity for electron-pair sharing that enables proton transfer to take place.



This equation for a simple acid-base neutralization shows how the Brønsted and Lewis definitions are really just different views of the same process. Take special note of the following points:

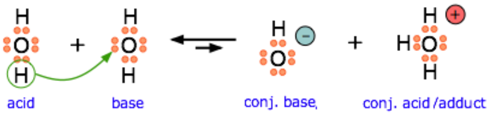
- The arrow shows the movement of a proton from the hydronium ion to the hydroxide ion.
- Note that the electron-pairs themselves do not move; they remain attached to their central atoms. The electron pair on the base is "donated" to the acceptor (the proton) only in the sense that it ends up being *shared* with the acceptor, rather than being the exclusive property of the oxygen atom in the hydroxide ion.
- Although the hydronium ion is the nominal Lewis acid here, it does not itself accept an electron pair, but acts merely as the source of the proton that coordinates with the Lewis base.

Note

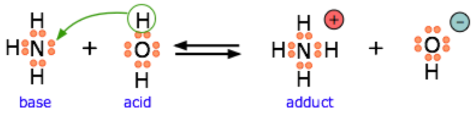
The point about the electron-pair remaining on the donor species is especially important to bear in mind. For one thing, it distinguishes a *Lewis acid-base reaction* from an *oxidation-reduction reaction*, in which a physical transfer of one or more electrons from donor to acceptor does occur.

The product of a Lewis acid-base reaction is known formally as an "**adduct**" or "complex", although we do not ordinarily use these terms for simple proton-transfer reactions such as the one in the above example. Here, the proton combines with the hydroxide ion to form the "adduct" H_2O. The following examples illustrate these points for some other proton-transfer reactions that you should already be familiar with.

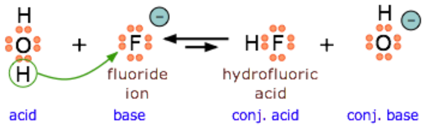
Another example, showing the autoprotolysis of water. Note that the conjugate acid is also the adduct.



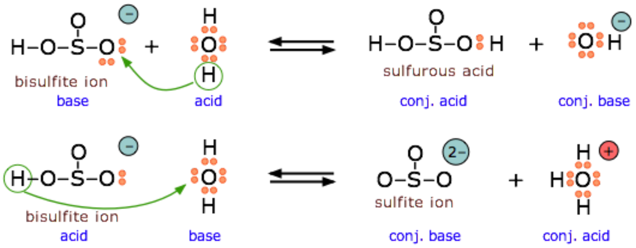
Ammonia is both a Brønsted and a Lewis base, owing to the unshared electron pair on the nitrogen. The reverse of this reaction represents the *hydrolysis* of the ammonium ion.



Because HF is a weak acid, fluoride salts behave as bases in aqueous solution. As a Lewis base, F^{-} accepts a proton from water, which is transformed into a hydroxide ion.



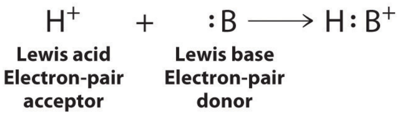
The bisulfite ion is *amphiprotic* and can act as an electron donor or acceptor.



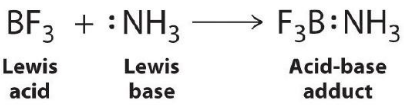
All Brønsted–Lowry bases (proton acceptors), such as OH^{-}, H_2O, and NH_3, are also electron-pair donors. Thus the Lewis definition of acids and bases does not contradict the Brønsted–Lowry definition. Rather, it expands the definition of acids to include substances other than the H^{+} ion.

Lewis Acid-Base Neutralization without Transferring Protons

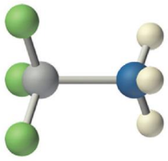
Electron-deficient molecules, such as BCl_3, contain less than an octet of electrons around one atom and have a strong tendency to gain an additional pair of electrons by reacting with substances that possess a lone pair of electrons. Lewis's definition, which is less restrictive than either the Brønsted–Lowry or the Arrhenius definition, grew out of his observation of this tendency. A general Brønsted–Lowry acid–base reaction can be depicted in Lewis electron symbols as follows:



The proton (H^+), which has no valence electrons, is a Lewis acid because it accepts a lone pair of electrons on the base to form a bond. The proton, however, is just one of many electron-deficient species that are known to react with bases. For example, neutral compounds of boron, aluminum, and the other Group 13 elements, which possess only six valence electrons, have a very strong tendency to gain an additional electron pair. Such compounds are therefore potent Lewis acids that react with an electron-pair donor such as ammonia to form an acid–base adduct, a new covalent bond, as shown here for boron trifluoride (BF_3):



The bond formed between a Lewis acid and a Lewis base is a **coordinate covalent bond** because both electrons are provided by only one of the atoms (N, in the case of $F_3B{:}NH_3$). After it is formed, however, a coordinate covalent bond behaves like any other covalent single bond.



Boron trifluoride-ammonia adduct

Species that are very weak Brønsted–Lowry bases can be relatively strong Lewis bases. For example, many of the group 13 trihalides are highly soluble in ethers (R–O–R′) because the oxygen atom in the ether contains two lone pairs of electrons, just as in H_2O. Hence the predominant species in solutions of electron-deficient trihalides in ether solvents is a Lewis acid–base adduct. A reaction of this type is shown in Figure $15.1.1$ for boron trichloride and diethyl ether:

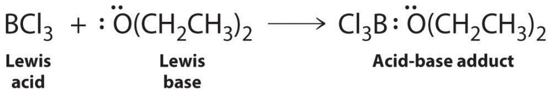
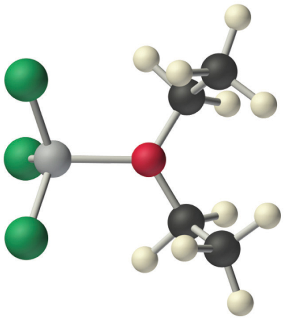


Figure $15.1.1$: Lewis Acid/Base reaction of boron trichloride and diethyl ether reaction

Note

- Electron-deficient molecules (those with less than an octet of electrons) are Lewis acids.
- The acid-base behavior of many compounds can be explained by their Lewis electron structures.

Many molecules with multiple bonds can act as Lewis acids. In these cases, the Lewis base typically donates a pair of electrons to form a bond to the central atom of the molecule, while a pair of electrons displaced from the multiple bond becomes a lone pair on a terminal atom.



Boron trichloride-diethyl ether adduct

Figure 15.1.2: The highly electronegative oxygen atoms pull electron density away from carbon, so the carbon atom acts as a Lewis acid. Arrows indicate the direction of electron flow.

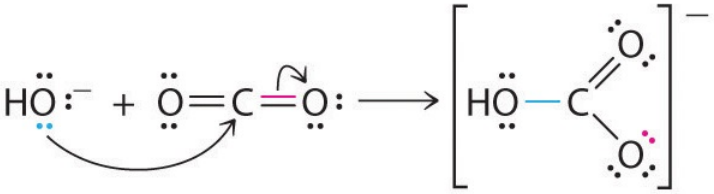


Figure 15.1.2 Lewis Acid/Base reaction of the hydroxide ion with carbon dioxide

Example 15.1.4

Identify the acid and the base in each Lewis acid–base reaction.

a. $BH_3 + (CH_3)_2S \rightarrow H_3B{:}S(CH_3)_2$
b. $CaO + CO_2 \rightarrow CaCO_3$
c. $BeCl_2 + 2\ Cl^- \rightarrow BeCl_4{}^{2-}$

Given: reactants and products

Asked for: identity of Lewis acid and Lewis base

Strategy:

In each equation, identify the reactant that is electron deficient and the reactant that is an electron-pair donor. The electron-deficient compound is the Lewis acid, whereas the other is the Lewis base.

Solution:

a. In BH_3, boron has only six valence electrons. It is therefore electron deficient and can accept a lone pair. Like oxygen, the sulfur atom in $(CH_3)_2S$ has two lone pairs. Thus $(CH_3)_2S$ donates an electron pair on sulfur to the boron atom of BH_3. The Lewis base is $(CH_3)_2S$, and the Lewis acid is BH_3.
b. As in the reaction shown in Equation 8.21, CO_2 accepts a pair of electrons from the O^{2-} ion in CaO to form the carbonate ion. The oxygen in CaO is an electron-pair donor, so CaO is the Lewis base. Carbon accepts a pair of electrons, so CO_2 is the Lewis acid.
c. The chloride ion contains four lone pairs. In this reaction, each chloride ion donates one lone pair to $BeCl_2$, which has only four electrons around Be. Thus the chloride ions are Lewis bases, and $BeCl_2$ is the Lewis acid.

Exercise 15.1.4A

Identify the acid and the base in each Lewis acid–base reaction.

a. $(CH_3)_2O + BF_3 \rightarrow (CH_3)_2O{:}BF_3$
b. $H_2O + SO_3 \rightarrow H_2SO_4$

Answer a

Lewis base: $(CH_3)_2O$; Lewis acid: BF_3

Answer b

Lewis base: H_2O; Lewis acid: SO_3

Exercise 15.1.4B

Here are several more examples of Lewis acid-base reactions that **cannot** be accommodated within the Brønsted or Arrhenius models. Identify the Lewis acid and Lewis base in each reaction.

a. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$
b. $SnS_2 + S^{2-} \rightarrow SnS_3^{2-}$
c. $Cd(CN)_2 + 2CN^- \rightarrow Cd(CN)_4^{2+}$
d. $AgCl + 2NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$
e. $Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$
f. $[Ni^{2+} + 6NH_3 \rightarrow Ni(NH_3)_5^{2+}$

Video 15.1.1: Overview of Lewis Acids and Bases

Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ C$$

Glossary

acid ionization

reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic

species that may either gain or lose a proton in a reaction

amphoteric

species that can act as either an acid or a base

autoionization

reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization

reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid

proton donor

Brønsted-Lowry base

proton acceptor

conjugate acid

substance formed when a base gains a proton

conjugate base

substance formed when an acid loses a proton

ion-product constant for water (K_w)

equilibrium constant for the autoionization of water

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- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

15.2: Properties of Acids and Bases in Aqueous Solutions

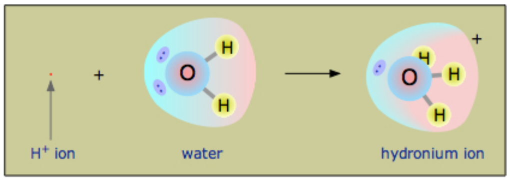
Learning Objectives

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- To know the relationship between acid or base strength and the magnitude of K_a, K_b, pK_a, and pK_b.
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

We now turn our attention to acid–base reactions to see how the concepts of chemical equilibrium and equilibrium constants can deepen our understanding of this kind of chemical behavior. We begin with a qualitative description of acid–base equilibria in terms of the Brønsted–Lowry model and then proceed to a quantitative description the following sections.

Free Hydrogen Ions do not Exist in Water

Owing to the overwhelming excess of H_2O molecules in aqueous solutions, a bare hydrogen ion has no chance of surviving in water. The hydrogen ion in aqueous solution is no more than a proton, a bare nucleus. Although it carries only a single unit of positive charge, this charge is concentrated into a volume of space that is only about a hundred-millionth as large as the volume occupied by the smallest atom. (Think of a pebble sitting in the middle of a sports stadium!) The resulting extraordinarily high *charge density* of the proton strongly attracts it to any part of a nearby atom or molecule in which there is an excess of negative charge. In the case of water, this will be the lone pair (unshared) electrons of the oxygen atom; the tiny proton will be buried within the lone pair and will form a shared-electron (coordinate) bond with it, creating a *hydronium ion*, H_3O^+. In a sense, H_2O is acting as a base here, and the product H_3O^+ is the conjugate acid of water:



Although other kinds of dissolved ions have water molecules bound to them more or less tightly, the interaction between H^+ and H_2O is so strong that writing "H^+*(aq)*" hardly does it justice, although it is formally correct. The formula H_3O^+ more adequately conveys the sense that it is both a molecule in its own right, and is also the conjugate acid of water. However, the equation

$$\text{HA} \rightarrow \text{H}^+ + \text{A}^-$$

is so much easier to write that chemists still use it to represent acid-base reactions in contexts in which the proton donor-acceptor mechanism does not need to be emphasized. Thus it is permissible to talk about "hydrogen ions" and use the formula H^+ in writing chemical equations as long as you remember that they are not to be taken literally in the context of aqueous solutions.

Interestingly, experiments indicate that the proton does not stick to a single H_2O molecule, but changes partners many times per second. This molecular promiscuity, a consequence of the uniquely small size and mass the proton, allows it to move through the solution by rapidly hopping from one H_2O molecule to the next, creating a new H_3O^+ ion as it goes. The overall effect is the same as if the H_3O^+ ion itself were moving. Similarly, a hydroxide ion, which can be considered to be a "proton hole" in the water, serves as a landing point for a proton from another H_2O molecule, so that the OH^- ion hops about in the same way.

The **hydronium** ion is an important factor when dealing with chemical reactions that occur in aqueous solutions. Because hydronium and hydroxide ions can "move without actually moving" and thus without having to plow their way through the solution by shoving aside water molecules as do other ions, solutions which are acidic or alkaline have extraordinarily high *electrical conductivities*. The hydronium ion has a trigonal pyramidal geometry and is composed of three hydrogen atoms and one oxygen atom. There is a lone pair of electrons on the oxygen giving it this shape. The bond angle between the atoms is 113 degrees.

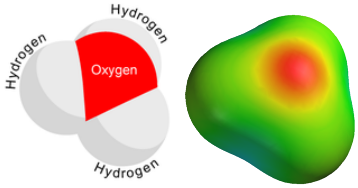


Figure 15.2.1. The picture above illustrates the electron density of hydronium. The red area represents oxygen; this is the area where the electrostatic potential is the highest and the electrons are most dense.

As H^+ ions are formed, they bond with H_2O molecules in the solution to form H_3O^+ (the hydronium ion). This is because hydrogen ions do not exist in aqueous solutions, but take the form the hydronium ion, H_3O^+. A reversible reaction is one in which the reaction goes both ways. In other words, the water molecules dissociate while the OH^- ions combine with the H^+ ions to form water. Water has the ability to attract H^+ ions because it is a polar molecule. This means that it has a partial charge, in this case the charge is negative. The partial charge is caused by the fact that oxygen is more electronegative than hydrogen. This means that in the bond between hydrogen and oxygen, oxygen "pulls" harder on the shared electrons thus causing a partial negative charge on the molecule and causing it to be attracted to the positive charge of H^+ to form **hydronium**. Another way to describe why the water molecule is considered polar is through the concept of dipole moment. The electron geometry of water is tetrahedral and the molecular geometry is bent. This bent geometry is asymmetrical, which causes the molecule to be polar and have a dipole moment, resulting in a partial charge.

The pH Scale

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is neutral if it contains equal concentrations of hydronium and hydroxide ions; acidic if it contains a greater concentration of hydronium ions than hydroxide ions; and basic if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities, the values of which may span many orders of magnitude, is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$\mathrm{pX} = -\log \mathrm{X} \tag{15.2.1}$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \tag{15.2.2}$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} \tag{15.2.3}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] \tag{15.2.4}$$

or

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}} \tag{15.2.5}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$\begin{aligned} K_\mathrm{w} &= [\mathrm{H_3O^+}][\mathrm{OH^-}] \\ -\log K_\mathrm{w} &= -\log([H_3O^+][OH^-]) \\ &= -\log[H_3O^+] + -\log[OH^-] \\ pK_w &= pH + pOH \end{aligned}$$

At 25 °C, the value of K_w is 1.0×10^{-14} and so:

$$14.00 = \text{pH} + \text{pOH} \tag{15.2.6}$$

The hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7}\ M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{15.2.7}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{15.2.8}$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities less than $1.0 \times 10^{-7}\ M$ (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7}\ M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} M, which corresponds to pH and pOH values of:

$$\begin{aligned} \text{pH} &= -\log[H_3O^+] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

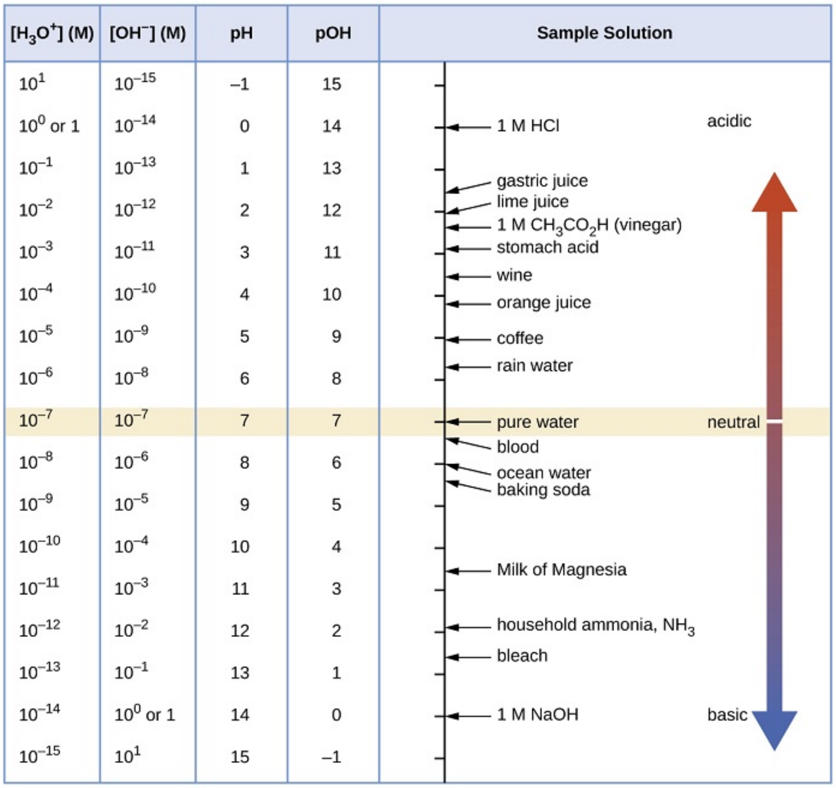
$$\begin{aligned} \text{pOH} &= -\log[OH^-] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table 15.2.1).

Table 15.2.1: Summary of Relations for Acidic, Basic and Neutral Solutions

Classification	Relative Ion Concentrations	pH at 25 °C	pH at 80 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7	pH < 6.31
neutral	$[H_3O^+] = [OH^-]$	pH = 7	pH = 6.31
basic	$[H_3O^+] < [OH^-]$	pH > 7	pH > 6.31

Figure 15.2.2 shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH, and gives values for these properties at standard temperatures for some common substances.



$[H_3O^+]$ (M)	$[OH^-]$ (M)	pH	pOH
10^{1}	10^{-15}	–1	15
10^{0} or 1	10^{-14}	0	14
10^{-1}	10^{-13}	1	13
10^{-2}	10^{-12}	2	12
10^{-3}	10^{-11}	3	11
10^{-4}	10^{-10}	4	10
10^{-5}	10^{-9}	5	9
10^{-6}	10^{-8}	6	8
10^{-7}	10^{-7}	7	7
10^{-8}	10^{-6}	8	6
10^{-9}	10^{-5}	9	5
10^{-10}	10^{-4}	10	4
10^{-11}	10^{-3}	11	3
10^{-12}	10^{-2}	12	2
10^{-13}	10^{-1}	13	1
10^{-14}	10^{0} or 1	14	0
10^{-15}	10^{1}	15	–1

Figure 15.2.2: The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

✓ Example 15.2.1: Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$?

Solution

$$\begin{aligned} \text{pH} &= -\log[H_3O^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) = 2.92 \end{aligned}$$

? Exercise 15.2.1

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$\text{CO}_{2(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{CO}_{3(aq)}$$

Air-saturated water has a hydronium ion concentration caused by the dissolved CO_2 of $2.0 \times 10^{-6}\ M$, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer

5.70

✓ Example 15.2.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3.

Solution

$$\begin{aligned}\mathrm{pH}=-\log[\mathrm{H_3O^+}] &= 7.3\\ [\mathrm{H_3O^+}] &= 10^{-7.3}\\ [\mathrm{H_3O^+}] &= 5\times10^{-8}\ M\end{aligned}$$

(On a calculator take the antilog, or the “inverse” log, of −7.3, or calculate $10^{-7.3}$.)

Exercise 15.2.2A

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Answer

12 M

This uses the definition of pH that we commonly use:

$$pH=-\log[H_3O^+]$$

So for this solution:

$$\begin{aligned}\mathrm{pH}=-\log[\mathrm{H_3O^+}] &= -1.07\\ [\mathrm{H_3O^+}] &= 10^{+1.07}\\ &= 12\ (\text{with significant figure})\end{aligned}$$

However, at this high concentration, the solution will be non-ideal and we have to use the proper definition in terms of hydronium activities

$$pH=-\log a\{H_3O^+\}$$

See this module for more details.

Exercise 15.2.2B

The ionization constant of water Kw at 37 °C is 2.42×10^{-14}. What is the pH for a neutral solution at this human physiological temperature? Is the water acidic, basic or neutral?

Answer

$$\mathrm{Kw}=[\mathrm{H_3O^+}][\mathrm{OH^-}]=2.42\times10^{-14}$$

and

$$\begin{aligned}[\mathrm{H_3O^+}]=[\mathrm{OH^-}] &= \sqrt{2.42\times10^{-14}}\\ &= 1.55\times10^{-7}\end{aligned}$$

$$pH=-\log[H_3O^+]=-\log 1.55\times10^{-7}=6.81 \tag{15.2.9}$$

If we use the definition of acidic systems like in Figure 15.2.2, then we would (incorrectly) argue the solution is acidic. However, since $[\mathrm{OH^-}]=[\mathrm{H_3O^+}]$, the solution is still neutral. This is only a strange idea, if one ignores the temperature dependence of Kw.

Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$\mathrm{H_2O_{(l)}+CO_{2(g)}\longrightarrow H_2CO_{3(aq)}} \tag{15.2.10}$$

$$\mathrm{H_2CO_{3(aq)}\rightleftharpoons H^+_{(aq)}+HCO^-_{3(aq)}} \tag{15.2.11}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2O_{(l)} + SO_{3(g)} \longrightarrow H_2SO_{4(aq)} \tag{15.2.12}$$

$$H_2SO_{4(aq)} \longrightarrow H^+_{(aq)} + HSO^-_{4(aq)} \tag{15.2.13}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of “roasting” ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

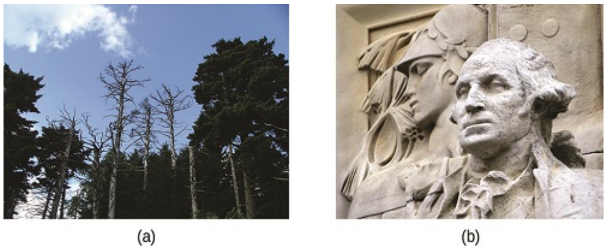


Figure 15.2.3: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr)

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 15.2.3). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure 15.2.4).

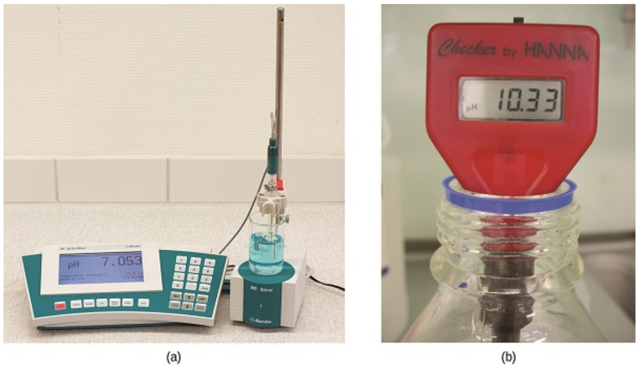


Figure 15.2.4: (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther).

✓ Example 15.2.3: Calculation of pOH

What are the pOH and the pH of a 0.0125-M solution of potassium hydroxide, KOH at 25 °C?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[OH^-]$ = 0.0125 M:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log 0.0125 \tag{15.2.14}$$

$$= -(-1.903) = 1.903 \tag{15.2.15}$$

The pH can be found from the pOH:

$$\mathrm{pH} + \mathrm{pOH} = 14.00 \tag{15.2.16}$$

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 1.903 = 12.10 \tag{15.2.17}$$

? Exercise 15.2.3

The hydronium ion concentration of vinegar is approximately $4 \times 10^{-3}\ M$ at 25 °C. What are the corresponding values of pOH and pH?

Answer

pOH = 11.6, pH = 2.4

The pH of a solution may also be visually estimated using colored indicators (Figure 15.2.5).

Figure 15.2.5: (a) A universal indicator assumes a different color in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-M solutions of progressively weaker acids: HCl (pH = l), CH_3CO_2H (pH = 3), and NH_4Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-M solutions of the progressively stronger bases: KCl (pH = 7), aniline, $C_6H_5NH_2$ (pH = 9), NH_3 (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa).

Summary

The concentration of hydronium ion in a solution of an acid in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of hydroxide ion in a solution of a base in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of H_3O^+ in a solution can be expressed as the pH of the solution; $\mathrm{pH} = -\log \mathrm{H_3O^+}$. The concentration of OH^- can be expressed as the pOH of the solution: $\mathrm{pOH} = -\log[\mathrm{OH^-}]$. In pure water, pH = 7.00 and pOH = 7.00

Key Equations

- $\mathrm{pH} = -\log[\mathrm{H_3O^+}]$
- $\mathrm{pOH} = -\log[\mathrm{OH^-}]$
- $[H_3O^+] = 10^{-\mathrm{pH}}$
- $[OH^-] = 10^{-\mathrm{pOH}}$
- pH + pOH = pK_w = 14.00 at 25 °C

Glossary

acidic

describes a solution in which $[H_3O^+] > [OH^-]$

basic

describes a solution in which $[H_3O^+] < [OH^-]$

neutral

describes a solution in which $[H_3O^+] = [OH^-]$

pH

logarithmic measure of the concentration of hydronium ions in a solution

pOH

logarithmic measure of the concentration of hydroxide ions in a solution

Contributors and Attributions

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

15.3: Acid and Base Strength

Learning Objectives

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{15.3.1}$$

Water is the base that reacts with the acid HA, $\mathrm{A^-}$ is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ when the acid ionizes in water; Figure $15.3.1$ lists several strong acids. A weak acid gives small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Figure $15.3.1$: Some of the common strong acids and bases are listed here.

Six Strong Acids		Six Strong Bases	
$\mathrm{HClO_4}$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\mathrm{Ca(OH)_2}$	calcium hydroxide
$\mathrm{HNO_3}$	nitric acid	$\mathrm{Sr(OH)_2}$	strontium hydroxide
$\mathrm{H_2SO_4}$	sulfuric acid	$\mathrm{Ba(OH)_2}$	barium hydroxide

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid HA:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{15.3.2}$$

we write the equation for the ionization constant as:

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \tag{15.3.3}$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is also the solvent. If the solution is assumed to be dilute, the activity of the water is approximated by the activity of pure water, which is defined as having a value of 1. The larger the K_a of an acid, the larger the concentration of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ relative to the concentration of the nonionized acid, HA. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase.

The following data on acid-ionization constants indicate the order of acid strength: $\mathrm{CH_3CO_2H} < \mathrm{HNO_2} < \mathrm{HSO_4^-}$

$$\begin{aligned}
\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \qquad & K_\mathrm{a} = 1.8 \times 10^{-5} \\
\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{NO_2^-}(aq) \qquad & K_\mathrm{a} = 4.6 \times 10^{-4} \\
\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(aq) &\rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq) \qquad & K_\mathrm{a} = 1.2 \times 10^{-2}
\end{aligned}$$

Another measure of the strength of an acid is its *percent ionization*. The percent ionization of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\%\text{ ionization} = \frac{[H_3O^+]_{eq}}{[HA]_0} \times 100\% \tag{15.3.4}$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

✓ Example 15.3.1: Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[H_3O^+]_{eq}}{[HNO_2]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq).$$

Since $10^{-pH} = [H_3O^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}\ M$, so that percent ionization (Equation 15.3.4) is:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

? Exercise 15.3.1

Calculate the percent ionization of a 0.10 *M* solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq) \tag{15.3.5}$$

Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yields 100% (or very nearly so) of OH^- and HB^+ when it reacts with water; Figure 15.3.1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq), \tag{15.3.6}$$

we write the equation for the ionization constant as:

$$K_b = \frac{[HB^+][OH^-]}{[B]} \tag{15.3.7}$$

where the concentrations are those at equilibrium. Again, we do not include $[H_2O]$ in the equation because water is the solvent. The chemical reactions and ionization constants of the three bases shown are:

$$\begin{aligned} NO_2^-(aq) + H_2O(l) &\rightleftharpoons HNO_2(aq) + OH^-(aq) && K_b = 2.17 \times 10^{-11} \\ CH_3CO_2^-(aq) + H_2O(l) &\rightleftharpoons CH_3CO_2H(aq) + OH^-(aq) && K_b = 5.6 \times 10^{-10} \\ NH_3(aq) + H_2O(l) &\rightleftharpoons NH_4^+(aq) + OH^-(aq) && K_b = 1.8 \times 10^{-5} \end{aligned}$$

A table of ionization constants of weak bases appears in Table E2. As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

Consider the ionization reactions for a conjugate acid-base pair, $HA - A^-$:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \tag{15.3.8}$$

with $K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$.

$$A^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HA(aq) \tag{15.3.9}$$

with $K_b = \dfrac{[HA][OH]}{[A^-]}$.

Adding these two chemical equations yields the equation for the autoionization for water:

$$\begin{aligned} HA\cancel{(aq)} + H_2O(l) + A^-\cancel{(aq)} + H_2O(l) &\rightleftharpoons H_3O^+(aq) + A^-\cancel{(aq)} + OH^-(aq) + HA\cancel{(aq)} \\ 2\,H_2O(l) &\rightleftharpoons H_3O^+(aq) + OH^-(aq) \end{aligned}$$

As shown in the previous chapter on equilibrium, the K expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations' K expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that:

$$K_a \times K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-] = K_w \tag{15.3.10}$$

For example, the acid ionization constant of acetic acid (CH_3COOH) is 1.8 × 10^{-5}, and the base ionization constant of its conjugate base, acetate ion (CH_3COO^-), is 5.6 × 10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_a \times K_b = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_w \tag{15.3.11}$$

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base, A^-, of the acid. If A^- is a strong base, any protons that are donated to water molecules are recaptured by A^-. Thus there is relatively little A^- and H_3O^+ in solution, and the acid, HA, is weak. If A^- is a weak base, water binds the protons more strongly, and the solution contains primarily A^- and H_3O^+—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure 15.3.2).

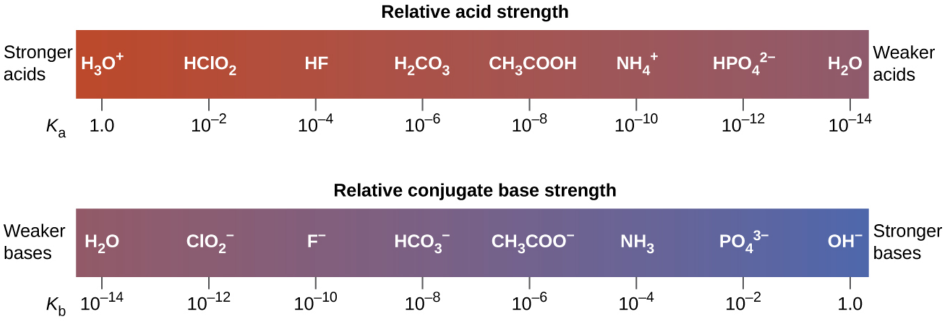
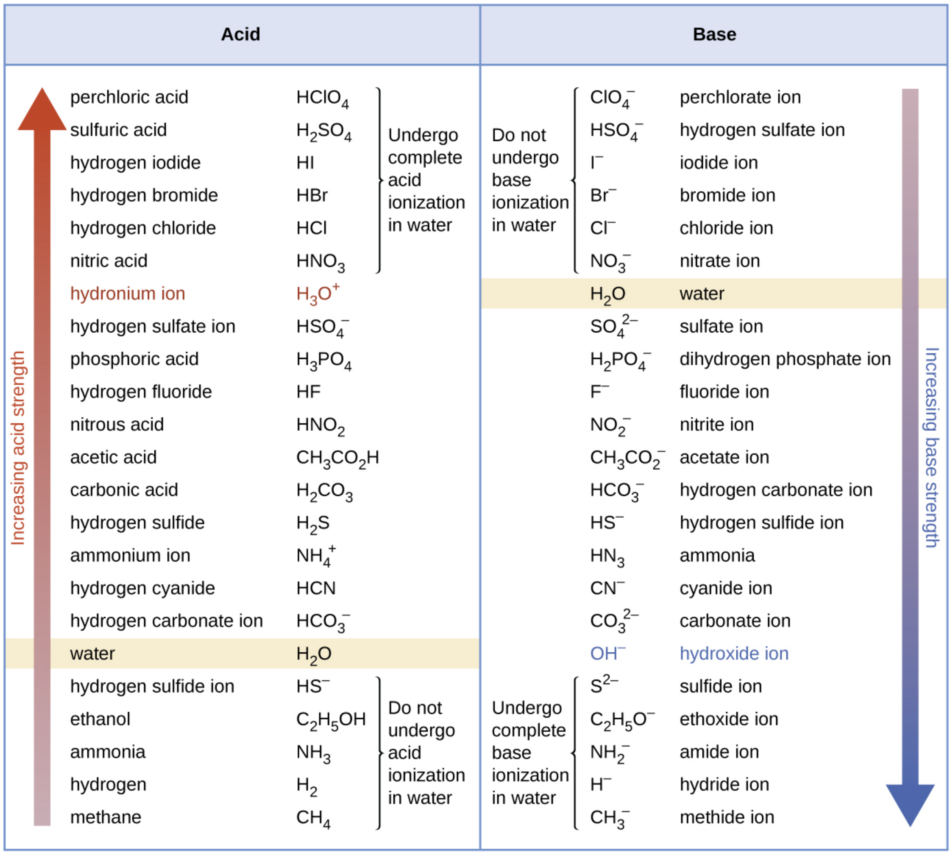


Figure 15.3.2: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure 15.3.3 lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.

The first six acids in Figure 15.3.3 are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure 15.3.3 form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure 15.3.3 exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.



Acid					Base
perchloric acid	$HClO_4$	Undergo complete acid ionization in water	Do not undergo base ionization in water	ClO_4^-	perchlorate ion
sulfuric acid	H_2SO_4			HSO_4^-	hydrogen sulfate ion
hydrogen iodide	HI			I^-	iodide ion
hydrogen bromide	HBr			Br^-	bromide ion
hydrogen chloride	HCl			Cl^-	chloride ion
nitric acid	HNO_3			NO_3^-	nitrate ion
hydronium ion	H_3O^+			H_2O	water
hydrogen sulfate ion	HSO_4^-			SO_4^{2-}	sulfate ion
phosphoric acid	H_3PO_4			$H_2PO_4^-$	dihydrogen phosphate ion
hydrogen fluoride	HF			F^-	fluoride ion
nitrous acid	HNO_2			NO_2^-	nitrite ion
acetic acid	CH_3CO_2H			$CH_3CO_2^-$	acetate ion
carbonic acid	H_2CO_3			HCO_3^-	hydrogen carbonate ion
hydrogen sulfide	H_2S			HS^-	hydrogen sulfide ion
ammonium ion	NH_4^+			HN_3	ammonia
hydrogen cyanide	HCN			CN^-	cyanide ion
hydrogen carbonate ion	HCO_3^-			CO_3^{2-}	carbonate ion
water	H_2O			OH^-	hydroxide ion
hydrogen sulfide ion	HS^-	Do not undergo acid ionization in water	Undergo complete base ionization in water	S^{2-}	sulfide ion
ethanol	C_2H_5OH			$C_2H_5O^-$	ethoxide ion
ammonia	NH_3			NH_2^-	amide ion
hydrogen	H_2			H^-	hydride ion
methane	CH_4			CH_3^-	methide ion

Figure 15.3.3: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure 15.3.3. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

✓ Example 15.3.2: The Product $K_a \times K_b = K_w$

Use the K_b for the nitrite ion, NO_2^-, to calculate the K_a for its conjugate acid.

Solution

K_b for NO_2^- is given in this section as 2.17×10^{-11}. The conjugate acid of NO_2^- is HNO_2; K_a for HNO_2 can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_a, we get:

$$\begin{aligned} K_\mathrm{a} &= \frac{K_\mathrm{w}}{K_\mathrm{b}} \\ &= \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}} \\ &= 4.6 \times 10^{-4} \end{aligned}$$

This answer can be verified by finding the K_a for HNO_2 in Table E1

? Exercise 15.3.2

We can determine the relative acid strengths of NH_4^+ and HCN by comparing their ionization constants. The ionization constant of HCN is given in Table E1 as 4.9 × 10^{-10}. The ionization constant of NH_4^+ is not listed, but the ionization constant of its conjugate base, NH_3, is listed as 1.8 × 10^{-5}. Determine the ionization constant of NH_4^+, and decide which is the stronger acid, HCN or NH_4^+.

Answer

NH_4^+ is the slightly stronger acid (K_a for NH_4^+ = 5.6 × 10^{-10}).

Summary

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion.

Key Equations

- $K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$
- $K_\mathrm{b} = \frac{[\mathrm{HB^+}][\mathrm{OH^-}]}{[\mathrm{B}]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w$ (at room temperature)

Glossary

acid ionization constant (K_a)
equilibrium constant for the ionization of a weak acid

base ionization constant (K_b)
equilibrium constant for the ionization of a weak base

leveling effect of water
any acid stronger than H_3O^+, or any base stronger than OH^- will react with water to form H_3O^+, or OH^-, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

percent ionization
ratio of the concentration of the ionized acid to the initial acid concentration, times 100

Contributors and Attributions

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15.4: Equilibria Involving Weak Acids and Bases

Learning Objectives

- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid, with the nonionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid ($\mathrm{CH_3CO_2H}$) is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)$$

giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules. We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment (Figure $15.4.1$). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{CH_3CO_2^-}]}{[\mathrm{CH_3CO_2H}]} = 1.8 \times 10^{-5}$$

Figure $15.4.1$: pH paper indicates that a 0.1-M solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[\mathrm{H_3O^+}]$ = 0.1 M. A 0.1-M solution of CH_3CO_2H (beaker on right) has a pH of 3 ($[\mathrm{H_3O^+}]$ = 0.001 M) because the weak acid CH_3CO_2H is only partially ionized. In this solution, $[\mathrm{H_3O^+}] < [\mathrm{CH_3CO_2H}]$. (credit: modification of work by Sahar Atwa)

Table $15.4.1$: Ionization Constants of Some Weak Acids

Ionization Reaction	K_a at 25 °C
$\mathrm{HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}}$	1.2 × 10^{-2}
$\mathrm{HF + H_2O \rightleftharpoons H_3O^+ + F^-}$	3.5 × 10^{-4}
$\mathrm{HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-}$	4.6 × 10^{-4}
$\mathrm{HNCO + H_2O \rightleftharpoons H_3O^+ + NCO^-}$	2 × 10^{-4}
$\mathrm{HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-}$	1.8 × 10^{-4}
$\mathrm{CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-}$	1.8 × 10^{-5}
$\mathrm{HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-}$	2.9 × 10^{-8}
$\mathrm{HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-}$	2.8 × 10^{-9}

Ionization Reaction	K_a at 25 °C
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9×10^{-10}

Table $15.4.1$ gives the ionization constants for several weak acids; additional ionization constants can be found in Table E1.

At equilibrium, a solution of a weak base in water is a mixture of the nonionized base, the conjugate acid of the weak base, and hydroxide ion with the nonionized base present in the greatest concentration. Thus, a weak base increases the hydroxide ion concentration in an aqueous solution (but not as much as the same amount of a strong base).

For example, a solution of the weak base trimethylamine, $(CH_3)_3N$, in water reacts according to the equation:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$$

This gives an equilibrium mixture with most of the base present as the nonionized amine. This equilibrium is analogous to that described for weak acids.

We can confirm by measuring the pH of an aqueous solution of a weak base of known concentration that only a fraction of the base reacts with water (Figure $15.4.2$). The remaining weak base is present as the unreacted form. The equilibrium constant for the ionization of a weak base, K_b, is called the **ionization constant** of the weak base, and is equal to the reaction quotient when the reaction is at equilibrium. For trimethylamine, at equilibrium:

$$K_\text{b} = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]}$$

Figure 15.4.2: pH paper indicates that a 0.1-M solution of NH_3 (left) is weakly basic. The solution has a pOH of 3 ($[OH^-] = 0.001$ M) because the weak base NH_3 only partially reacts with water. A 0.1-M solution of NaOH (right) has a pOH of 1 because NaOH is a strong base (credit: modification of work by Sahar Atwa).

The ionization constants of several weak bases are given in Table $15.4.2$ and Table E2.

Table 15.4.2: Ionization Constants of Some Weak Bases

Ionization Reaction	**K_b at 25 °C**
$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$	5.9×10^{-4}
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.4×10^{-4}
$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$	6.3×10^{-5}
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
$C_6H_5NH_2 + H_2O \rightleftharpoons C_6N_5NH_3^+ + OH^-$	4.3×10^{-10}

✓ Example $15.4.3$: Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar; that's why it tastes sour. At equilibrium, a solution contains $[CH_3CO_2H]$ = 0.0787 M and $[H_3O^+] = [CH_3CO_2^-] = 0.00118\ M$. What is the value of K_a for acetic acid?

Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by “HomeSpot HQ”/Flickr)

Solution

We are asked to calculate an equilibrium constant from equilibrium concentrations. At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

$$\begin{aligned} K_a &= \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} \\ &= \frac{(0.00118)(0.00118)}{0.0787} \\ &= 1.77 \times 10^{-5} \end{aligned}$$

Exercise 15.4.3

What is the equilibrium constant for the ionization of the HSO_4^- ion, the weak acid used in some household cleansers:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

In one mixture of $NaHSO_4$ and Na_2SO_4 at equilibrium, $[H_3O^+]$ = 0.027 *M*; $[HSO_4^-] = 0.29\ M$; and $[SO_4^{2-}] = 0.13\ M$.

Answer

K_a for $HSO_4^- = 1.2 \times \times 10^{-2}$

Example 15.4.4: Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2]$ = 0.050 *M*, $[C_8H_{10}N_4O_2H^+]$ = 5.0 × 10^{-3} *M*, and $[OH^-]$ = 2.5 × 10^{-3} *M*?

Solution

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq)$$

so

$$K_b = \frac{[C_8H_{10}N_4O_2H^+][OH^-]}{[C_8H_{10}N_4O_2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

Exercise 15.4.4

What is the equilibrium constant for the ionization of the HPO_4^{2-} ion, a weak base:

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$$

In a solution containing a mixture of NaH_2PO_4 and Na_2HPO_4 at equilibrium with:

- $[OH^-] = 1.3 \times 10^{-6}\,M$
- $[H_2PO_4^-]$=0 $\cdot$ 042 M and
- $[HPO_4^{2-}]$=0 $\cdot$ 341 M.

Answer

K_b for $HPO_4^{2-} = 1.6 \times 10^{-7}$

Example 15.4.5: Determination of K_a or K_b from pH

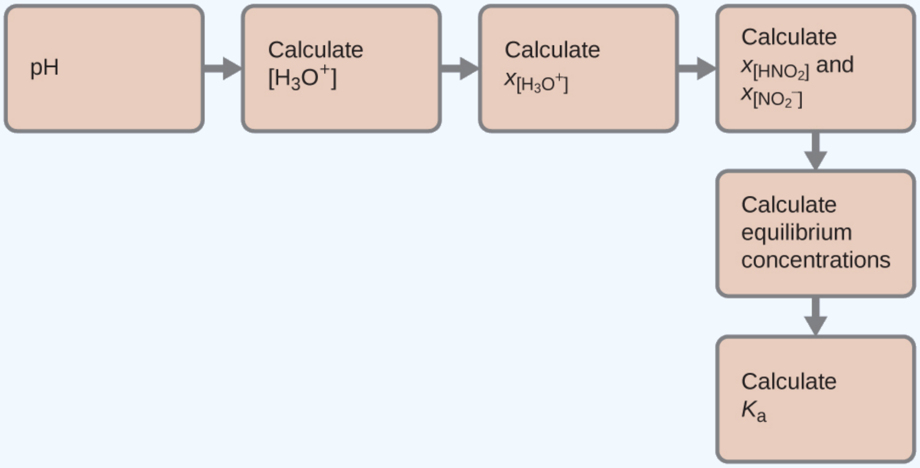
The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

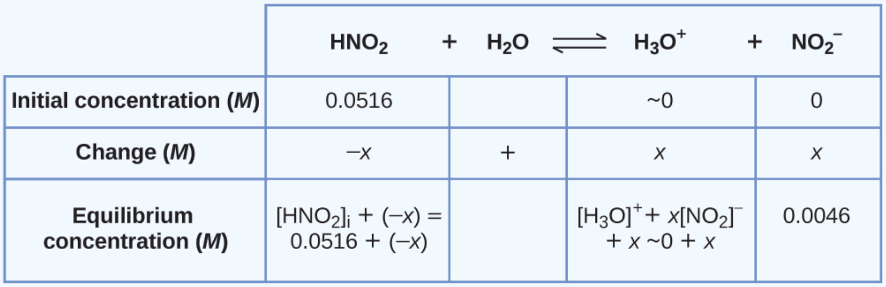
Solution

We determine an equilibrium constant starting with the initial concentrations of HNO_2, H_3O^+, and NO_2^- as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the concentration of hydronium ion.)

We can solve this problem with the following steps in which *x* is a change in concentration of a species in the reaction:



We can summarize the various concentrations and changes as shown here (the concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its concentration):



	HNO_2	$+ \; H_2O \rightleftharpoons$	H_3O^+	$+ \; NO_2^-$
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	$-x$	+	x	x
Equilibrium concentration (*M*)	$[HNO_2]_i + (-x) =$ $0.0516 + (-x)$		$[H_3O]^+ + x[NO_2]^-$ $+ x \sim 0 + x$	0.0046

To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate $[H_3O^+]$, the equilibrium concentration of H_3O^+, from the pH:

$$[H_3O^+] = 10^{-2.34} = 0.0046\,M$$

The change in concentration of H_3O^+, $x_{[H_3O^+]}$, is the difference between the equilibrium concentration of H_3O^+, which we determined from the pH, and the initial concentration, $[H_3O^+]_i$. The initial concentration of H_3O^+ is its concentration in pure water, which is so much less than the final concentration that we approximate it as zero (~0).

The change in concentration of NO_2^- is equal to the change in concentration of $[H_3O^+]$. For each 1 mol of H_3O^+ that forms, 1 mol of NO_2^- forms. The equilibrium concentration of HNO_2 is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

	HNO_2	+ H_2O	$\rightleftharpoons$ H_3O^+	+ NO_2^-
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	$-x$	+	x = 0.0046	x = 0.0046
Equilibrium concentration (*M*)	0.0470		0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

Exercise 15.4.5

The pH of a solution of household ammonia, a 0.950-*M* solution of NH_3, is 11.612. What is K_b for NH_3.

Answer

$$K_b = 1.8 \times 10^{-5}$$

Example 15.4.6: Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid, HCO_2H, is the irritant that causes the body's reaction to ant stings.

The pain of an ant's sting is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH in a 0.534-*M* solution of formic acid?

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq) \quad K_a = 1.8 \times 10^{-4}$$

Solution

1. Determine x and equilibrium concentrations. The equilibrium expression is:

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq)$$

The concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its change in concentration when setting up the ICE table.

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

	HCO_2H +	H_2O $\rightleftharpoons$	H_3O^+
Initial concentration (*M*)	0.534	~0	0
Change (*M*)	−*x*	*x*	*x*
Equilibrium concentration (*M*)	0.534 + (−*x*)	0 + *x* = *x*	0 + *x* = *x*

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$\begin{aligned} K_a &= 1.8 \times 10^{-4} = \frac{[H_3O^+][HCO_2^-]}{[HCO_2H]} \\ &= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4} \end{aligned}$$

Now solve for x. Because the initial concentration of acid is reasonably large and K_a is very small, we assume that $x << 0.534$, which *permits* us to simplify the denominator term as $(0.534 - x) = 0.534$. This gives:

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solve for x as follows:

$$\begin{aligned} x^2 &= 0.534 \times (1.8 \times 10^{-4}) \\ &= 9.6 \times 10^{-5} \\ x &= \sqrt{9.6 \times 10^{-5}} \\ &= 9.8 \times 10^{-3} \end{aligned}$$

To check the assumption that x is small compared to 0.534, we calculate:

$$\begin{aligned} \frac{x}{0.534} &= \frac{9.8 \times 10^{-3}}{0.534} \\ &= 1.8 \times 10^{-2} \; (1.8\% \text{ of } 0.534) \end{aligned}$$

x is less than 5% of the initial concentration; the assumption is valid.

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change in that concentration as indicated in the last line of the table:

$$\begin{aligned} [H_3O^+] &= 0 + x = 0 + 9.8 \times 10^{-3}\ M. \\ &= 9.8 \times 10^{-3}\ M \end{aligned}$$

The pH of the solution can be found by taking the negative log of the $[H_3O^+]$, so:

$$pH = -\log(9.8 \times 10^{-3}) = 2.01$$

? Exercise 15.4.6: acetic acid

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$

Hint

Determine $[CH_3CO_2^-]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or $\frac{[CH_3CO_2^-]}{[CH_3CO_2H]_{\text{initial}}} \times 100$.

Answer

percent ionization = 1.3%

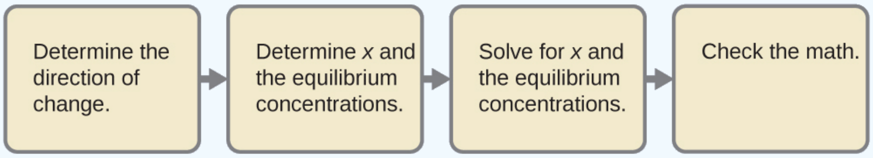
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

Example 15.4.7: Equilibrium Concentrations in a Solution of a Weak Base

Find the concentration of hydroxide ion in a 0.25-*M* solution of trimethylamine, a weak base:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq) \quad K_b = 6.3 \times 10^{-5}$$

Solution This problem requires that we calculate an equilibrium concentration by determining concentration changes as the ionization of a base goes to equilibrium. The solution is approached in the same way as that for the ionization of formic acid in Example 15.4.6. The reactants and products will be different and the numbers will be different, but the logic will be the same:



1. Determine x and equilibrium concentrations. The table shows the changes and concentrations:

	$(CH_3)_3N$ +	H_2O ⇌	$(CH_3)_3NH^+$ +	OH^-
Initial concentration (*M*)	0.25		0	~0
Change (*M*)	−*x*		*x*	*x*
Equilibrium concentration (*M*)	0.25 + (−*x*)		0 + *x*	~0 + *x*

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{0.25 - x =} 6.3 \times 10^{-5}$$

If we assume that *x* is small relative to 0.25, then we can replace (0.25 − *x*) in the preceding equation with 0.25. Solving the simplified equation gives:

$$x = 4.0 \times 10^{-3}$$

This change is less than 5% of the initial concentration (0.25), so the assumption is justified.

Recall that, for this computation, x is equal to the equilibrium concentration of *hydroxide ion* in the solution (see earlier tabulation):

$$([OH^-] = 0 + x = x = 4.0 \times 10^{-3}\ M$$

$$= 4.0 \times 10^{-3}\ M$$

Then calculate pOH as follows:

$$pOH = -\log(4.3 \times 10^{-3}) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$pH + pOH = pK_w = 14.00$$

permits the computation of pH:

$$pH = 14.00 - pOH = 14.00 - 2.37 = 11.60$$

Check the work. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

? Exercise 15.4.7

a. Show that the calculation in Step 2 of this example gives an x of 4.3 × 10^{-3} and the calculation in Step 3 shows K_b = 6.3 × 10^{-5}.

b. Find the concentration of hydroxide ion in a 0.0325-*M* solution of ammonia, a weak base with a K_b of 1.76 × 10^{-5}. Calculate the percent ionization of ammonia, the fraction ionized × 100, or $\frac{[NH_4^+]}{[NH_3]} \times 100\%$

Answer a

$7.56 \times 10^{-4}\ M$, 2.33%

Answer b

2.33%

Some weak acids and weak bases ionize to such an extent that the simplifying assumption that x is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

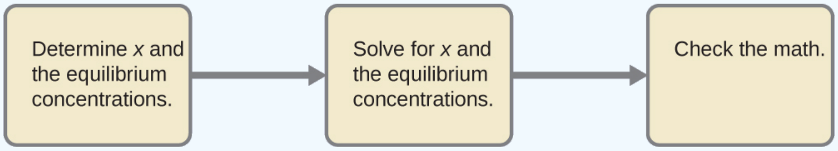
✓ Example 15.4.8: Equilibrium Concentrations in a Solution of a Weak Acid

Sodium bisulfate, $NaHSO_4$, is used in some household cleansers because it contains the HSO_4^- ion, a weak acid. What is the pH of a 0.50-*M* solution of HSO_4^-?

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \quad K_a = 1.2 \times 10^{-2}$$

Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of HSO_4^- so that we can use $[H_3O^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



1. *Determine x and equilibrium concentrations.* This table shows the changes and concentrations:

	HSO_4^- +	H_2O ⇌	H_3O^+ +	SO_4^{2-}
Initial concentration (*M*)	0.50		~0	0
Change (*M*)	−*x*		*x*	*x*
Equilibrium concentration (*M*)	0.50 + (−*x*) = 0.50 − *x*)		0 + *x* = *x*	0 + *x* = *x*

2. *Solve for x and the concentrations.*

As we begin solving for x, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of x.

At equilibrium:

$$K_a = 1.2 \times 10^{-2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(x)(x)}{0.50 - x}$$

If we assume that x is small and approximate $(0.50 - x)$ as 0.50, we find:

$$x = 7.7 \times 10^{-2}$$

When we check the assumption, we confirm:

$$\frac{x}{[HSO_4^-]_i} \overset{?}{\leq} 0.05$$

which for this system is

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15(15\%)$$

The value of x is not less than 5% of 0.50, so the assumption is not valid. We need the quadratic formula to find x.

The equation:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

gives

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2} x = x^{2+}$$

or

$$x^{2+} + 1.2 \times 10^{-2} x - 6.0 \times 10^{-3} = 0$$

This equation can be solved using the quadratic formula. For an equation of the form

$$ax^{2+} + bx + c = 0,$$

x is given by the quadratic equation:

$$x = \frac{-b \pm \sqrt{b^{2+} - 4ac}}{2a}$$

In this problem, $a = 1$, $b = 1.2 \times 10^{-3}$, and $c = -6.0 \times 10^{-3}$.

Solving for x gives a negative root (which cannot be correct since concentration cannot be negative) and a positive root:

$$x = 7.2 \times 10^{-2}$$

Now determine the hydronium ion concentration and the pH:

$$\begin{aligned}[H_3O^+] &= 0 + x = 0 + 7.2 \times 10^{-2}\ M \\ &= 7.2 \times 10^{-2}\ M\end{aligned}$$

The pH of this solution is:

$$\text{pH} = -\log[H_3O^+] = -\log 7.2 \times 10^{-2} = 1.14$$

? Exercise 15.4.8

a. Show that the quadratic formula gives $x = 7.2 \times 10^{-2}$.
b. Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq) \quad K_b = 2.5 \times 10^{-4}$$

Hint

> It will be necessary to convert $[OH^-]$ to $[H_3O^+]$ or pOH to pH toward the end of the calculation.
>
> **Answer**
>
> pH 11.16

The Relative Strengths of Strong Acids and Bases

Strong acids, such as HCl, HBr, and HI, all exhibit the same strength in water. The water molecule is such a strong base compared to the conjugate bases Cl^-, Br^-, and I^- that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find HCl, HBr, and HI differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol (a weaker base than water), the extent of ionization increases in the order $HCl < HBr < HI$, and so HI is demonstrated to be the strongest of these acids. The inability to discern differences in strength among strong acids dissolved in water is known as the leveling effect of water.

Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, O^{2-}, and the amide ion, NH_2^-, are such strong bases that they react completely with water:

$$O^{2-}(aq) + H_2O(l) \longrightarrow OH^-(aq) + OH^-(aq) \tag{15.4.1}$$

$$NH_2^-(aq) + H_2O(l) \longrightarrow NH_3(aq) + OH^-(aq) \tag{15.4.2}$$

Thus, O^{2-} and NH_2^- appear to have the same base strength in water; they both give a 100% yield of hydroxide ion.

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is $HF < HCl < HBr < HI$. Likewise, for group 16, the order of increasing acid strength is $H_2O < H_2S < H_2Se < H_2Te$. Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $CH_4 < NH_3 < H_2O < HF$; across the third row, it is $SiH_4 < PH_3 < H_2S < HCl$ (see Figure 15.4.3).

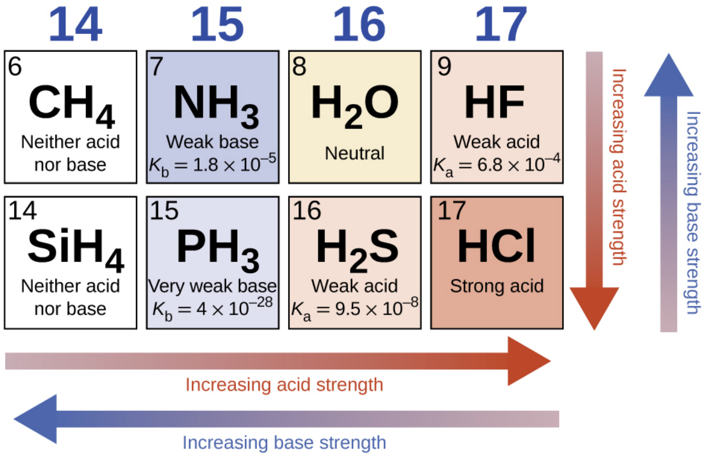
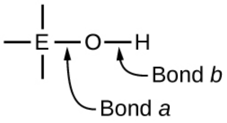


Figure 15.4.3: As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

Compounds containing oxygen and one or more hydroxyl (OH) groups can be acidic, basic, or amphoteric, depending on the position in the periodic table of the central atom E, the atom bonded to the hydroxyl group. Such compounds have the general formula $O_nE(OH)_m$, and include sulfuric acid, $O_2S(OH)_2$, sulfurous acid, $OS(OH)_2$, nitric acid, O_2NOH, perchloric acid, O_3ClOH, aluminum hydroxide, $Al(OH)_3$, calcium hydroxide, $Ca(OH)_2$, and potassium hydroxide, KOH:



If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic −OH groups that are called oxyacids.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3, or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure $15.4.4$).

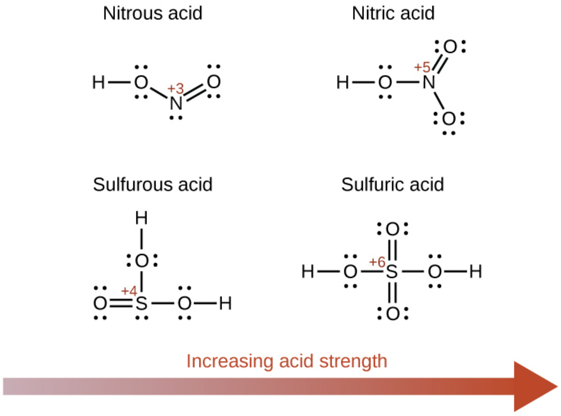


Figure 15.4.4: As the oxidation number of the central atom E increases, the acidity also increases.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate $\mathrm{Al(H_2O)_3(OH)_3}$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $\mathrm{Al(H_2O)_3(OH)_3}$, is converted into the soluble ion, $\mathrm{[Al(H_2O)_2(OH)_4]^-}$, by reaction with hydroxide ion:

$$\mathrm{[Al(H_2O)_3(OH)_3]}(aq) + \mathrm{OH^-}(aq) \rightleftharpoons \mathrm{H_2O}(l) + \mathrm{[Al(H_2O)_2(OH)_4]^-}(aq)$$

In this reaction, a proton is transferred from one of the aluminum-bound $\mathrm{H_2O}$ molecules to a hydroxide ion in solution. The $\mathrm{Al(H_2O)_3(OH)_3}$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion $\mathrm{[Al(H_2O)_6]^{3+}}$ by reaction with hydronium ion:

$$3\,\mathrm{H_3O^+}(aq) + \mathrm{Al(H_2O)_3(OH)_3}(aq) \rightleftharpoons \mathrm{Al(H_2O)_6^{3+}}(aq) + 3\,\mathrm{H_2O}(l)$$

In this case, protons are transferred from hydronium ions in solution to $\mathrm{Al(H_2O)_3(OH)_3}$, and the compound functions as a base.

Summary

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion. The strengths of the binary acids increase from left to right across a period of the periodic table ($CH_4 < NH_3 < H_2O < HF$), and they increase down a group (HF < HCl < HBr < HI). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases ($H_2SO_3 < H_2SO_4$). The strengths of oxyacids also increase as the electronegativity of the central element increases [$H_2SeO_4 < H_2SO_4$].

Key Equations

- $K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$
- $K_\mathrm{b} = \frac{[\mathrm{HB^+}][\mathrm{OH^-}]}{[\mathrm{B}]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w \text{ (at room temperature)}$
- $\text{Percent ionization} = \frac{[\mathrm{H_3O^+}]_\mathrm{eq}}{[\mathrm{HA}]_0} \times 100$

Glossary

acid ionization constant (K_a)

equilibrium constant for the ionization of a weak acid

base ionization constant (K_b)

equilibrium constant for the ionization of a weak base

leveling effect of water

any acid stronger than $\mathrm{H_3O^+}$, or any base stronger than OH^- will react with water to form $\mathrm{H_3O^+}$, or OH^-, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

oxyacid

compound containing a nonmetal and one or more hydroxyl groups

percent ionization

ratio of the concentration of the ionized acid to the initial acid concentration, times 100

15.5: Buffer Solutions

Learning Objectives

- To understand how adding a common ion affects the position of an acid–base equilibrium.
- To know how to use the Henderson-Hasselbalch approximation to calculate the pH of a buffer.

Buffers are solutions that maintain a relatively constant pH when an acid or a base is added. They therefore protect, or "buffer," other molecules in solution from the effects of the added acid or base. Buffers contain either a weak acid (HA) and its conjugate base (A^-) or a weak base (B) and its conjugate acid (BH^+), and they are critically important for the proper functioning of biological systems. In fact, every biological fluid is buffered to maintain its physiological pH.

The Common Ion Effect: Weak Acids Combined with Conjugate Bases

To understand how buffers work, let's look first at how the ionization equilibrium of a weak acid is affected by adding either the conjugate base of the acid or a strong acid (a source of $\mathrm{H^+}$). Le Chatelier's principle can be used to predict the effect on the equilibrium position of the solution. A typical buffer used in biochemistry laboratories contains acetic acid and a salt such as sodium acetate. The dissociation reaction of acetic acid is as follows:

$$\mathrm{CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)} \tag{15.5.1}$$

and the equilibrium constant expression is as follows:

$$K_a = \frac{\mathrm{[H^+][CH_3COO^-]}}{\mathrm{[CH_3CO_2H]}} \tag{15.5.2}$$

Sodium acetate ($\mathrm{CH_3CO_2Na}$) is a strong electrolyte that ionizes completely in aqueous solution to produce $\mathrm{Na^+}$ and $\mathrm{CH_3CO_2^-}$ ions. If sodium acetate is added to a solution of acetic acid, Le Chatelier's principle predicts that the equilibrium in Equation 15.5.1 will shift to the left, consuming some of the added $\mathrm{CH_3COO^-}$ and some of the $\mathrm{H^+}$ ions originally present in solution.

Because $\mathrm{Na^+}$ is a **spectator ion**, it has no effect on the position of the equilibrium and can be ignored. The addition of sodium acetate produces a new equilibrium composition, in which $\mathrm{[H^+]}$ is less than the initial value. Because $\mathrm{[H^+]}$ has decreased, the pH will be higher. Thus adding a salt of the conjugate base to a solution of a weak acid increases the pH. This makes sense because sodium acetate is a base, and adding any base to a solution of a weak acid should increase the pH.

If we instead add a strong acid such as HCl to the system, $\mathrm{[H^+]}$ increases. Once again the equilibrium is temporarily disturbed, but the excess $\mathrm{H^+}$ ions react with the conjugate base ($\mathrm{CH_3CO_2^-}$), whether from the parent acid or sodium acetate, to drive the equilibrium to the left. The net result is a new equilibrium composition that has a lower $\mathrm{[CH_3CO_2^-]}$ than before. In both cases, only the equilibrium composition has changed; the ionization constant K_a for acetic acid remains the same. Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium, in this case $\mathrm{CH_3CO_2^-}$, will therefore shift the equilibrium in the direction that reduces the concentration of the common ion. The shift in equilibrium is via the common ion effect.

> *Adding a common ion to a system at equilibrium affects the equilibrium composition, but not the ionization constant.*

Example 15.5.1

A 0.150 M solution of formic acid at 25°C (pKa = 3.75) has a pH of 2.28 and is 3.5% ionized.

a. Is there a change to the pH of the solution if enough solid sodium formate is added to make the final formate concentration 0.100 M (assume that the formic acid concentration does not change)?
b. What percentage of the formic acid is ionized if 0.200 M HCl is added to the system?

Given: solution concentration and pH, pK_a, and percent ionization of acid; final concentration of conjugate base or strong acid added

Asked for: pH and percent ionization of formic acid

Strategy:

A. Write a balanced equilibrium equation for the ionization equilibrium of formic acid. Tabulate the initial concentrations, the changes, and the final concentrations.
B. Substitute the expressions for the final concentrations into the expression for Ka. Calculate $[H^+]$ and the pH of the solution.
C. Construct a table of concentrations for the dissociation of formic acid. To determine the percent ionization, determine the anion concentration, divide it by the initial concentration of formic acid, and multiply the result by 100.

Solution:

A Because sodium formate is a strong electrolyte, it ionizes completely in solution to give formate and sodium ions. The Na^+ ions are spectator ions, so they can be ignored in the equilibrium equation. Because water is both a much weaker acid than formic acid and a much weaker base than formate, the acid–base properties of the solution are determined solely by the formic acid ionization equilibrium:

$$HCO_2H(aq) \rightleftharpoons HCO_2^-(aq) + H^+(aq)$$

The initial concentrations, the changes in concentration that occur as equilibrium is reached, and the final concentrations can be tabulated.

Final Concentration

ICE	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
Initial	0.150	1.00×10^{-7}	0.100
Change	−x	+x	+x
Equilibrium	(0.150 − x)	x	(0.100 + x)

B We substitute the expressions for the final concentrations into the equilibrium constant expression and make our usual simplifying assumptions, so

$$\begin{aligned} K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} &= \frac{(x)(0.100+x)}{0.150-x} \\ &\approx \frac{x(0.100)}{0.150} \\ &\approx 10^{-3.75} \\ &\approx 1.8 \times 10^{-4} \end{aligned}$$

Rearranging and solving for x,

$$\begin{aligned} x &= (1.8 \times 10^{-4}) \times \frac{0.150\ M}{0.100\ M} \\ &= 2.7 \times 10^{-4} \\ &= [H^+] \end{aligned}$$

The value of x is small compared with 0.150 or 0.100 M, so our assumption about the extent of ionization is justified. Moreover,

$$K_aC_{HA} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5}$$

which is greater than 1.0×10^{-6}, so again, our assumption is justified. The final pH is:

$$pH = -\log(2.7 \times 10^{-4}) = 3.57$$

compared with the initial value of 2.29. Thus adding a salt containing the conjugate base of the acid has increased the pH of the solution, as we expect based on Le Chatelier’s principle; the stress on the system has been relieved by the consumption of H^+ ions, driving the equilibrium to the left.

C Because HCl is a strong acid, it ionizes completely, and chloride is a spectator ion that can be neglected. Thus the only relevant acid–base equilibrium is again the dissociation of formic acid, and initially the concentration of formate is zero. We can construct a table of initial concentrations, changes in concentration, and final concentrations.

$$HCO_2H(aq) \leftrightharpoons H^+(aq) + HCO_2^-(aq)$$

initial concentrations, changes in concentration, and final concentrations

	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
initial	0.150	0.200	0
change	−x	+x	+x
final	(0.150 − x)	(0.200 + x)	x

To calculate the percentage of formic acid that is ionized under these conditions, we have to determine the final $[HCO_2^-]$. We substitute final concentrations into the equilibrium constant expression and make the usual simplifying assumptions, so

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(0.200 + x)(x)}{0.150 - x} \approx \frac{x(0.200)}{0.150} = 1.80 \times 10^{-4}$$

Rearranging and solving for x,

$$\begin{aligned} x &= (1.80 \times 10^{-4}) \times \frac{0.150\ M}{0.200\ M} \\ &= 1.35 \times 10^{-4} = [HCO_2^-] \end{aligned}$$

Once again, our simplifying assumptions are justified. The percent ionization of formic acid is as follows:

$$\text{percent ionization} = \frac{1.35 \times 10^{-4}\ M}{0.150\ M} \times 100\% = 0.0900\%$$

Adding the strong acid to the solution, as shown in the table, decreased the percent ionization of formic acid by a factor of approximately 38 (3.45%/0.0900%). Again, this is consistent with Le Chatelier's principle: adding H^+ ions drives the dissociation equilibrium to the left.

? Exercise 15.5.1

A 0.225 M solution of ethylamine ($CH_3CH_2NH_2$ with $pK_b = 3.19$) has a pH of 12.08 and a percent ionization of 5.4% at 20°C. Calculate the following:

a. the pH of the solution if enough solid ethylamine hydrochloride ($EtNH_3Cl$) is added to make the solution 0.100 M in $EtNH_3^+$
b. the percentage of ethylamine that is ionized if enough solid $NaOH$ is added to the original solution to give a final concentration of 0.050 M $NaOH$

Answer a

11.16

Answer b

1.3%

A Video Discussing the Common Ion Effect: The Common Ion Effecr(opens in new window) [youtu.be]

The Common Ion Effect: Weak Bases Combined with Conjugate Acids

Now let’s suppose we have a buffer solution that contains equimolar concentrations of a weak base (B) and its conjugate acid (BH^+). The general equation for the ionization of a weak base is as follows:

$$B(aq) + H_2O(l) \leftrightharpoons BH^+(aq) + OH^-(aq) \tag{15.5.3}$$

If the equilibrium constant for the reaction as written in Equation 15.5.3 is small, for example $K_b = 10^{-5}$, then the equilibrium constant for the reverse reaction is very large: $K = \dfrac{1}{K_b} = 10^5$. Adding a strong base such as OH^- to the solution therefore causes the equilibrium in Equation 15.5.3 to shift to the left, consuming the added OH^-. As a result, the OH^- ion concentration in solution remains relatively constant, and the pH of the solution changes very little. Le Chatelier’s principle predicts the same outcome: when the system is stressed by an increase in the OH^- ion concentration, the reaction will proceed to the left to counteract the stress.

If the pK_b of the base is 5.0, the pK_a of its conjugate acid is

$$pK_a = pK_w - pK_b = 14.0 – 5.0 = 9.0.$$

Thus the equilibrium constant for ionization of the conjugate acid is even smaller than that for ionization of the base. The ionization reaction for the conjugate acid of a weak base is written as follows:

$$BH^+(aq) + H_2O(l) \leftrightharpoons B(aq) + H_3O^+(aq) \tag{15.5.4}$$

Again, the equilibrium constant for the reverse of this reaction is very large: K = 1/K_a = 10^9. If a strong acid is added, it is neutralized by reaction with the base as the reaction in Equation 15.5.4 shifts to the left. As a result, the H^+ ion concentration does not increase very much, and the pH changes only slightly. In effect, a buffer solution behaves somewhat like a sponge that can absorb H^+ and OH^- ions, thereby preventing large changes in pH when appreciable amounts of strong acid or base are added to a solution.

Buffers are characterized by the pH range over which they can maintain a more or less constant pH and by their buffer capacity, the amount of strong acid or base that can be absorbed before the pH changes significantly. Although the useful pH range of a buffer depends strongly on the chemical properties of the weak acid and weak base used to prepare the buffer (i.e., on K), its buffer capacity depends solely on the concentrations of the species in the buffered solution. The more concentrated the buffer solution, the greater its buffer capacity. As illustrated in Figure 15.5.1, when $NaOH$ is added to solutions that contain different concentrations of an acetic acid/sodium acetate buffer, the observed change in the pH of the buffer is inversely proportional to the concentration of the buffer. If the buffer capacity is 10 times larger, then the buffer solution can absorb 10 times more strong acid or base before undergoing a significant change in pH.

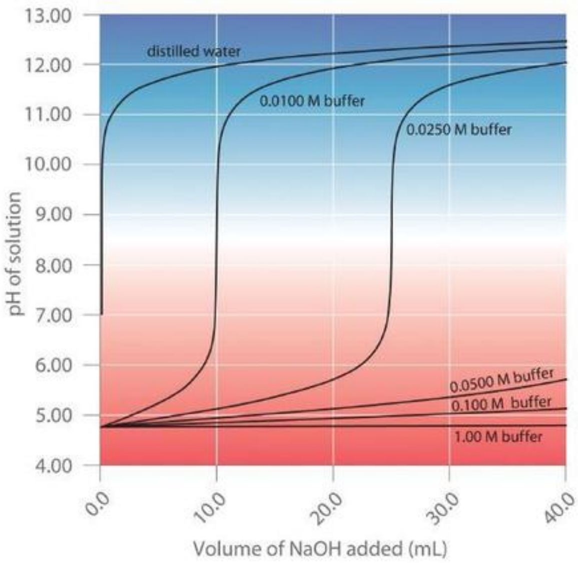


Figure 15.5.1: Effect of Buffer Concentration on the Capacity of a Buffer. (CC BY-SA-NC; Anonymous by request)
Graph of pH of solution against volume of NaOH added. Six different buffer concentrations are plotted.

A buffer maintains a relatively constant pH when acid or base is added to a solution. The addition of even tiny volumes of 0.10 M $NaOH$ to 100.0 mL of distilled water results in a very large change in pH. As the concentration of a 50:50 mixture of sodium acetate/acetic acid buffer in the solution is increased from 0.010 M to 1.00 M, the change in the pH produced by the addition of the same volume of $NaOH$ solution decreases steadily. For buffer concentrations of at least 0.500 M, the addition of even 25 mL of the $NaOH$ solution results in only a relatively small change in pH.

Calculating the pH of a Buffer

The pH of a buffer can be calculated from the concentrations of the weak acid and the weak base used to prepare it, the concentration of the conjugate base and conjugate acid, and the pK_a or pK_b of the weak acid or weak base. The procedure is analogous to that used in Example 15.5.1 to calculate the pH of a solution containing known concentrations of formic acid and formate.

An alternative method frequently used to calculate the pH of a buffer solution is based on a rearrangement of the equilibrium equation for the dissociation of a weak acid. The simplified ionization reaction is $HA \rightleftharpoons H^+ + A^-$, for which the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{15.5.5}$$

This equation can be rearranged as follows:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \tag{15.5.6}$$

Taking the logarithm of both sides and multiplying both sides by −1,

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right) \tag{15.5.7}$$

$$= -\log K_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{15.5.8}$$

Replacing the negative logarithms in Equation 15.5.8,

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{15.5.9}$$

or, more generally,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{15.5.10}$$

Equation 15.5.9 and Equation 15.5.10 are both forms of the Henderson-Hasselbalch approximation, named after the two early 20th-century chemists who first noticed that this rearranged version of the equilibrium constant expression provides an easy way to calculate the pH of a buffer solution. In general, the validity of the Henderson-Hasselbalch approximation may be limited to solutions whose concentrations are at least 100 times greater than their K_a values.

There are three special cases where the Henderson-Hasselbalch approximation is easily interpreted without the need for calculations:

- $[base] = [acid]$: Under these conditions,

  $$\frac{[base]}{[acid]} = 1$$

  in Equation 15.5.10. Because $\log 1 = 0$,

  $$pH = pK_a$$

  regardless of the actual concentrations of the acid and base. Recall that this corresponds to the midpoint in the titration of a weak acid or a weak base.
- $[base]/[acid] = 10$: In Equation 15.5.10, because $\log 10 = 1$,

  $$pH = pK_a + 1.$$

- $[base]/[acid] = 100$: In Equation 15.5.10, because $\log 100 = 2$,

  $$pH = pK_a + 2.$$

Each time we increase the [base]/[acid] ratio by 10, the pH of the solution increases by 1 pH unit. Conversely, if the [base]/[acid] ratio is 0.1, then pH = pK_a − 1. Each additional factor-of-10 decrease in the [base]/[acid] ratio causes the pH to decrease by 1 pH unit.

> If [base] = [acid] for a buffer, then pH = pK_a. Changing this ratio by a factor of 10 either way changes the pH by ±1 unit.

✓ Example 15.5.2

What is the pH of a solution that contains

a. 0.135 M HCO_2H and 0.215 M HCO_2Na? (The pK_a of formic acid is 3.75.)
b. 0.0135 M HCO_2H and 0.0215 M HCO_2Na?
c. 0.119 M pyridine and 0.234 M pyridine hydrochloride? (The pK_b of pyridine is 8.77.)

Given: concentration of acid, conjugate base, and pK_a; concentration of base, conjugate acid, and pK_b

Asked for: pH

Strategy:

Substitute values into either form of the Henderson-Hasselbalch approximation (Equations 15.5.9 or 15.5.10) to calculate the pH.

Solution:

According to the Henderson-Hasselbalch approximation (Equation 15.5.9), the pH of a solution that contains both a weak acid and its conjugate base is

$$pH = pK_a + \log([A-]/[HA]).$$

A

Inserting the given values into the equation,

$$\begin{aligned} pH &= 3.75 + \log\left(\frac{0.215}{0.135}\right) \\ &= 3.75 + \log 1.593 \\ &= 3.95 \end{aligned}$$

This result makes sense because the $[A^-]/[HA]$ ratio is between 1 and 10, so the pH of the buffer must be between the pK_a (3.75) and $pK_a + 1$, or 4.75.

B

This is identical to part (a), except for the concentrations of the acid and the conjugate base, which are 10 times lower. Inserting the concentrations into the Henderson-Hasselbalch approximation,

$$\begin{aligned} pH &= 3.75 + \log\left(\frac{0.0215}{0.0135}\right) \\ &= 3.75 + \log 1.593 \\ &= 3.95 \end{aligned}$$

This result is identical to the result in part (a), which emphasizes the point that the pH of a buffer depends only on the ratio of the concentrations of the conjugate base and the acid, not on the magnitude of the concentrations. Because the [A$^-$]/[HA] ratio is the same as in part (a), the pH of the buffer must also be the same (3.95).

C

In this case, we have a weak base, pyridine (Py), and its conjugate acid, the pyridinium ion (HPy^+). We will therefore use Equation 15.5.10, the more general form of the Henderson-Hasselbalch approximation, in which "base" and "acid" refer to the appropriate species of the conjugate acid–base pair. We are given [base] = [Py] = 0.119 M and $[acid] = [HPy^+] = 0.234\ M$. We also are given $pK_b = 8.77$ for pyridine, but we need pK_a for the pyridinium ion. Recall from Equation 16.23 that the pK_b of a weak base and the pK_a of its conjugate acid are related:

$$pK_a + pK_b = pK_w.$$

Thus pK_a for the pyridinium ion is $pK_w - pK_b = 14.00 - 8.77 = 5.23$. Substituting this pK_a value into the Henderson-Hasselbalch approximation,

$$\begin{aligned} pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \\ &= 5.23 + \log\left(\frac{0.119}{0.234}\right) \\ &= 5.23\ - 0.294 \\ &= 4.94 \end{aligned}$$

Once again, this result makes sense: the $[B]/[BH^+]$ ratio is about 1/2, which is between 1 and 0.1, so the final pH must be between the pK_a (5.23) and $pK_a - 1$, or 4.23.

? Exercise 15.5.2

What is the pH of a solution that contains

a. 0.333 M benzoic acid and 0.252 M sodium benzoate?
b. 0.050 M trimethylamine and 0.066 M trimethylamine hydrochloride?

The pK_a of benzoic acid is 4.20, and the pK_b of trimethylamine is also 4.20.

Answer a

4.08

Answer b

9.68

A Video Discussing Using the Henderson Hasselbalch Equation: Using the Henderson Hasselbalch Equation(opens in new window) [youtu.be] (opens in new window)

The Henderson-Hasselbalch approximation ((Equation 15.5.9) can also be used to calculate the pH of a buffer solution after adding a given amount of strong acid or strong base, as demonstrated in Example $15.5.3$.

Example $15.5.3$

The buffer solution in Example $15.5.2$ contained 0.135 M $\mathrm{HCO_2H}$ and 0.215 M $\mathrm{HCO_2Na}$ and had a pH of 3.95.

a. What is the final pH if 5.00 mL of 1.00 M HCl are added to 100 mL of this solution?
b. What is the final pH if 5.00 mL of 1.00 M $NaOH$ are added?

Given: composition and pH of buffer; concentration and volume of added acid or base

Asked for: final pH

Strategy:

A. Calculate the amounts of formic acid and formate present in the buffer solution using the procedure from Example $15.5.1$. Then calculate the amount of acid or base added.
B. Construct a table showing the amounts of all species after the neutralization reaction. Use the final volume of the solution to calculate the concentrations of all species. Finally, substitute the appropriate values into the Henderson-Hasselbalch approximation (Equation 15.5.10) to obtain the pH.

Solution:

The added HCl (a strong acid) or NaOH (a strong base) will react completely with formate (a weak base) or formic acid (a weak acid), respectively, to give formic acid or formate and water. We must therefore calculate the amounts of formic acid and formate present after the neutralization reaction.

A We begin by calculating the millimoles of formic acid and formate present in 100 mL of the initial pH 3.95 buffer:

$$100\ \cancel{mL}\left(\frac{0.135\,mmol\ \mathrm{HCO_2H}}{\cancel{mL}}\right)=13.5\,mmol\,\mathrm{HCO_2H}$$

$$100\ \cancel{mL}\left(\frac{0.215\,mmol\ \mathrm{HCO_2^-}}{\cancel{mL}}\right)=21.5\,mmol\,\mathrm{HCO_2^-}$$

The millimoles of $\mathrm{H^+}$ in 5.00 mL of 1.00 M HCl is as follows:

$$5.00\ \cancel{mL}\left(\frac{1.00\,mmol\ \mathrm{H^+}}{\cancel{mL}}\right)=5\,mmol\,\mathrm{H^+}$$

B Next, we construct a table of initial amounts, changes in amounts, and final amounts:

$$\mathrm{HCO^{2\,-}(aq) + H^+(aq) \rightleftharpoons HCO_2H(aq)}$$

initial amounts, changes in amounts, and final amounts:

	$HCO^{2-}(aq)$	$H^+(aq)$	$HCO_2H(aq)$
Initial	21.5 mmol	5.00 mmol	13.5 mmol
Change	−5.00 mmol	−5.00 mmol	+5.00 mmol
Final	16.5 mmol	∼0 mmol	18.5 mmol

The final amount of H^+ in solution is given as "∼0 mmol." For the purposes of the stoichiometry calculation, this is essentially true, but remember that the point of the problem is to calculate the final $[H^+]$ and thus the pH. We now have all the information we need to calculate the pH. We can use either the lengthy procedure of Example 15.5.1 or the Henderson–Hasselbach approximation. Because we have performed many equilibrium calculations in this chapter, we'll take the latter approach. The Henderson-Hasselbalch approximation requires the concentrations of HCO_2^- and HCO_2H, which can be calculated using the number of millimoles (n) of each and the total volume (VT). Substituting these values into the Henderson-Hasselbalch approximation (Equation 15.5.10):

$$\begin{aligned} pH &= pK_a + \log\left(\frac{[HCO_2^-]}{[HCO_2H]}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}/V_f}{n_{HCO_2H}/V_f}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \end{aligned}$$

Because the total volume appears in both the numerator and denominator, it cancels. We therefore need to use only the ratio of the number of millimoles of the conjugate base to the number of millimoles of the weak acid. So

$$\begin{aligned} pH &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \\ &= 3.75 + \log\left(\frac{16.5\ mmol}{18.5\ mmol}\right) \\ &= 3.75 - 0.050 = 3.70 \end{aligned}$$

Once again, this result makes sense on two levels. First, the addition of HClhas decreased the pH from 3.95, as expected. Second, the ratio of HCO_2^- to HCO_2H is slightly less than 1, so the pH should be between the pK_a and pK_a − 1.

A The procedure for solving this part of the problem is exactly the same as that used in part (a). We have already calculated the numbers of millimoles of formic acid and formate in 100 mL of the initial pH 3.95 buffer: 13.5 mmol of HCO_2H and 21.5 mmol of HCO_2^-. The number of millimoles of OH^- in 5.00 mL of 1.00 M $NaOH$ is as follows:

B With this information, we can construct a table of initial amounts, changes in amounts, and final amounts.

$$\mathrm{HCO_2H(aq) + OH^-(aq) \rightleftharpoons HCO_2^-(aq) + H_2O(l)}$$

initial amounts, changes in amounts, and final amounts

	$HCO_2H(aq)$	OH^-	$HCO_2^-(aq)$
Initial	13.5 mmol	5.00 mmol	21.5 mmol
Change	−5.00 mmol	−5.00 mmol	+5.00 mmol
Final	8.5 mmol	∼0 mmol	26.5 mmol

The final amount of OH^- in solution is not actually zero; this is only approximately true based on the stoichiometric calculation. We can calculate the final pH by inserting the numbers of millimoles of both HCO_2^- and HCO_2H into the simplified Henderson-Hasselbalch expression used in part (a) because the volume cancels:

$$\begin{aligned} pH &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \\ &= 3.75 + \log\left(\frac{26.5\ mmol}{8.5\ mmol}\right) \\ &= 3.75 + 0.494 = 4.24 \end{aligned}$$

Once again, this result makes chemical sense: the pH has increased, as would be expected after adding a strong base, and the final pH is between the pK_a and pK_a + 1, as expected for a solution with a HCO_2^-/HCO_2H ratio between 1 and 10.

? Exercise 15.5.3

The buffer solution from Example $15.5.2$ contained 0.119 M pyridine and 0.234 M pyridine hydrochloride and had a pH of 4.94.

a. What is the final pH if 12.0 mL of 1.5 M NaOH are added to 250 mL of this solution?
b. What is the final pH if 12.0 mL of 1.5 M HCl are added?

Answer a

5.30

Answer b

4.42

Only the amounts (in moles or millimoles) of the acidic and basic components of the buffer are needed to use the Henderson-Hasselbalch approximation, not their concentrations.

A Video Discussing the Change in pH with the Addition of a Strong Acid to a Buffer: The Change in pH with the Addition of a Strong Acid to a Buffer(opens in new window) [youtu.be]

The Change in pH with the Addition of a Strong Base to a Buffer:

The Change in pH with the Addition of a Strong Base to a Buffer (opens in new window) [youtu.be]

The results obtained in Example $15.5.3$ and its corresponding exercise demonstrate how little the pH of a well-chosen buffer solution changes despite the addition of a significant quantity of strong acid or strong base. Suppose we had added the same amount of HCl or $NaOH$ solution to 100 mL of an unbuffered solution at pH 3.95 (corresponding to 1.1×10^{-4} M HCl). In this case, adding 5.00 mL of 1.00 M HCl would lower the final pH to 1.32 instead of 3.70, whereas adding 5.00 mL of 1.00 M $NaOH$ would raise the final pH to 12.68 rather than 4.24. (Try verifying these values by doing the calculations yourself.) Thus the presence of a buffer significantly increases the ability of a solution to maintain an almost constant pH.

> *The most effective buffers contain **equal** concentrations of an acid and its conjugate base.*

A buffer that contains approximately equal amounts of a weak acid and its conjugate base in solution is equally effective at neutralizing either added base or added acid. This is shown in Figure $15.5.2$ for an acetic acid/sodium acetate buffer. Adding a given amount of strong acid shifts the system along the horizontal axis to the left, whereas adding the same amount of strong base shifts the system the same distance to the right. In either case, the change in the ratio of $CH_3CO_2^-$ to CH_3CO_2H from 1:1 reduces the buffer capacity of the solution.

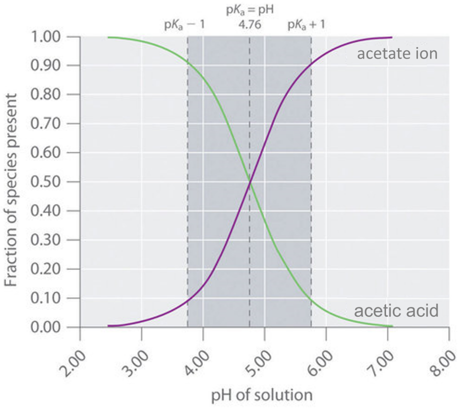


Figure 15.5.2: Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid. The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable concentrations of both species are present (pH 3.76–5.76, corresponding to $pH = pK_a \pm 1$). (CC BY-SA-NC; Anonymous by request)

Graph of mole fraction against pH of solution. The green line is acetic acid and the purple line is the acetate ion.

A Video Discussing The Buffer Region: The Buffer Region (opens in new window) [youtu.be]

The Relationship between Titrations and Buffers

There is a strong correlation between the effectiveness of a buffer solution and the titration curves discussed in Section 16.5. Consider the schematic titration curve of a weak acid with a strong base shown in Figure 15.5.3. As indicated by the labels, the region around pK_a corresponds to the midpoint of the titration, when approximately half the weak acid has been neutralized. This portion of the titration curve corresponds to a buffer: it exhibits the smallest change in pH per increment of added strong base, as shown by the nearly horizontal nature of the curve in this region. The nearly flat portion of the curve extends only from approximately a pH value of 1 unit less than the pK_a to approximately a pH value of 1 unit greater than the pK_a, which is why buffer solutions usually have a pH that is within ±1 pH units of the pK_a of the acid component of the buffer.

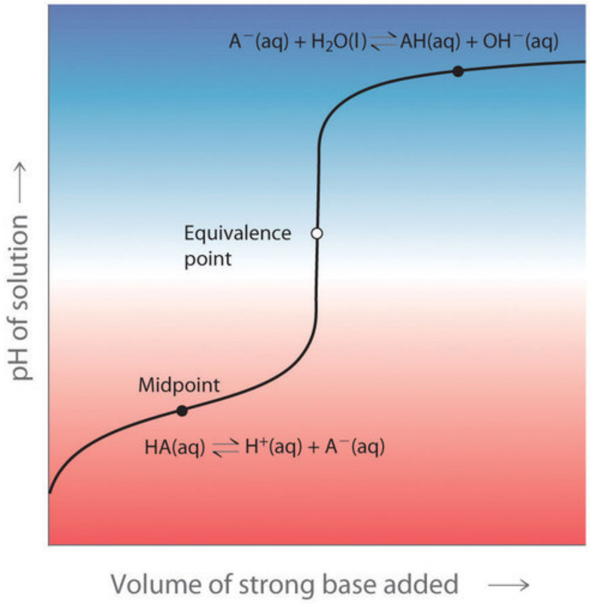


Figure 15.5.3: The Relationship between Titration Curves and Buffers. (CC BY-SA-NC; Anonymous by request)

Titration curves graph pH of solution against volume of strong base added. On the curve we look for the midpoints and equivalence points.

This schematic plot of pH for the titration of a weak acid with a strong base shows the nearly flat region of the titration curve around the midpoint, which corresponds to the formation of a buffer. At the lower left, the pH of the solution is determined by the equilibrium for dissociation of the weak acid; at the upper right, the pH is determined by the equilibrium for reaction of the conjugate base with water.

In the region of the titration curve at the lower left, before the midpoint, the acid–base properties of the solution are dominated by the equilibrium for dissociation of the weak acid, corresponding to K_a. In the region of the titration curve at the upper right, after the midpoint, the acid–base properties of the solution are dominated by the equilibrium for reaction of the conjugate base of the weak acid with water, corresponding to K_b. However, we can calculate either K_a or K_b from the other because they are related by K_w.

Blood: A Most Important Buffer

Metabolic processes produce large amounts of acids and bases, yet organisms are able to maintain an almost constant internal pH because their fluids contain buffers. This is not to say that the pH is uniform throughout all cells and tissues of a mammal. The internal pH of a red blood cell is about 7.2, but the pH of most other kinds of cells is lower, around 7.0. Even within a single cell, different compartments can have very different pH values. For example, one intracellular compartment in white blood cells has a pH of around 5.0.

Because no single buffer system can effectively maintain a constant pH value over the entire physiological range of approximately pH 5.0 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the $\mathrm{CO_2/HCO_3^-}$ system, which dominates the buffering action of blood plasma.

The acid–base equilibrium in the $\mathrm{CO_2/HCO_3^-}$ buffer system is usually written as follows:

$$\mathrm{H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)} \tag{15.5.11}$$

with $K_a = 4.5 \times 10^{-7}$ and $pK_a = 6.35$ at 25°C. In fact, Equation 15.5.11 is a grossly oversimplified version of the $\mathrm{CO_2/HCO_3^-}$ system because a solution of $\mathrm{CO_2}$ in water contains only rather small amounts of H_2CO_3. Thus Equation 15.5.11does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C.

As shown in Equation 15.5.12, $\mathrm{CO_2}$ is in equilibrium with $\mathrm{H_2CO_3}$, but the equilibrium lies far to the left, with an $\mathrm{H_2CO_3/CO_2}$ ratio less than 0.01 under most conditions:

$$\mathrm{CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)} \tag{15.5.12}$$

with $K' = 4.0 \times 10^{-3}$ at 37°C. The true pK_a of carbonic acid at 37°C is therefore 3.70, not 6.35, corresponding to a K_a of 2.0×10^{-4}, which makes it a much stronger acid than Equation 15.5.11 suggests. Adding Equation 15.5.11 and Equation 15.5.12and canceling $\mathrm{H_2CO_3}$ from both sides give the following overall equation for the reaction of $\mathrm{CO_2}$ with water to give a proton and the bicarbonate ion:

$$\mathrm{CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)} \tag{15.5.13}$$

with $K' = 4.0 \times 10^{-3} (37^\circ C)$

$$\mathrm{H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)} \tag{15.5.14}$$

with $K_a = 2.0 \times 10^{-4} (37^\circ C)$

$$\mathrm{CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)} \tag{15.5.15}$$

with $K = 8.0 \times 10^{-7} (37^\circ C)$

The K value for the reaction in Equation 15.5.15is the product of the true ionization constant for carbonic acid (K_a) and the equilibrium constant (K) for the reaction of $\mathrm{CO_2(aq)}$ with water to give carbonic acid. The equilibrium equation for the reaction of $\mathrm{CO_2}$ with water to give bicarbonate and a proton is therefore

$$K = \frac{\mathrm{[H^+][HCO_3^-]}}{\mathrm{[CO_2]}} = 8.0 \times 10^{-7} \tag{15.5.16}$$

The presence of a gas in the equilibrium constant expression for a buffer is unusual. According to **Henry’s law**,

$$\mathrm{[CO_2]} = kP_{\mathrm{CO_2}}$$

where k is the Henry’s law constant for $\mathrm{CO_2}$, which is $3.0 \times 10^{-5}\ M/mmHg$ at 37°C. Substituting this expression for $\mathrm{[CO_2]}$ in Equation 15.5.16,

$$K = \frac{\mathrm{[H^+][HCO_3^-]}}{(3.0 \times 10^{-5}\ M/mmHg)(P_{\mathrm{CO_2}})}$$

where $P_{\mathrm{CO_2}}$ is in mmHg. Taking the negative logarithm of both sides and rearranging,

$$pH = 6.10 + \log\left(\frac{[\mathrm{HCO_3^-}]}{(3.0\times10^{-5} M/mm\ Hg)\ (P_{\mathrm{CO_2}})}\right) \tag{15.5.17}$$

Thus the pH of the solution depends on both the $\mathrm{CO_2}$ pressure over the solution and $[\mathrm{HCO_3^-}]$. Figure 15.5.4 plots the relationship between pH and $[\mathrm{HCO_3^-}]$ under physiological conditions for several different values of $P_{\mathrm{CO_2}}$, with normal pH and $[\mathrm{HCO_3^-}]$ values indicated by the dashed lines.

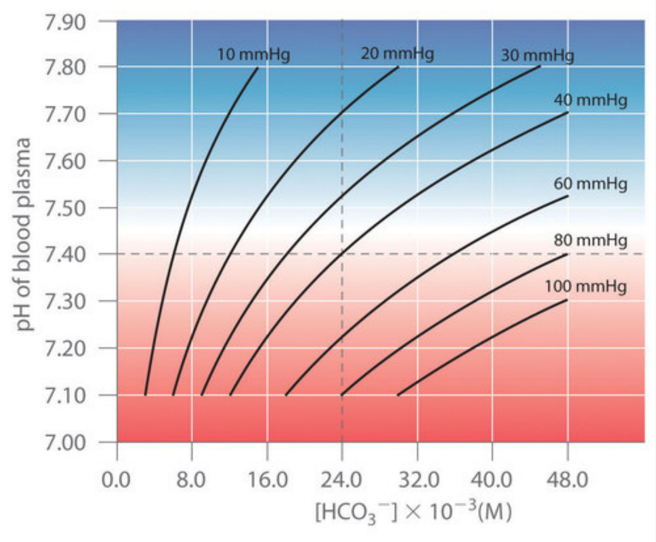


Figure 15.5.4: Buffering in Blood: pH versus $[\mathrm{HCO_3^-}]$ Curves for Buffers with Different Values of $P_{\mathrm{CO_2}}$. Only those combinations of pH and $[\mathrm{HCO_3^-}]$ that lie on a given line are allowed for the particular value of $P_{\mathrm{CO_2}}$ indicated. Normal values of blood plasma pH and $[\mathrm{HCO_3^-}]$ are indicated by dashed lines. (CC BY-SA-NC; Anonymous by request)

According to Equation 15.5.17, adding a strong acid to the $\mathrm{CO_2/HCO_3^-}$ system causes $[\mathrm{HCO_3^-}]$ to decrease as $\mathrm{HCO_3^-}$ is converted to $\mathrm{CO_2}$. Excess $\mathrm{CO_2}$ is released in the lungs and exhaled into the atmosphere, however, so there is essentially no change in $P_{\mathrm{CO_2}}$. Because the change in $[\mathrm{HCO_3^-}]/P_{CO_2}$ is small, Equation 15.5.17 predicts that the change in pH will also be rather small. Conversely, if a strong base is added, the $\mathrm{OH^-}$ reacts with $\mathrm{CO_2}$ to form $\mathrm{HCO_3^-}$, but $\mathrm{CO_2}$ is replenished by the body, again limiting the change in both $[\mathrm{HCO_3^-}]/P_{\mathrm{CO_2}}$ and pH. The $\mathrm{CO_2/HCO_3^-}$ buffer system is an example of an open system, in which the total concentration of the components of the buffer change to keep the pH at a nearly constant value.

If a passenger steps out of an airplane in Denver, Colorado, for example, the lower $P_{\mathrm{CO_2}}$ at higher elevations (typically 31 mmHg at an elevation of 2000 m versus 40 mmHg at sea level) causes a shift to a new pH and $[\mathrm{HCO_3^-}]$. The increase in pH and decrease in $[\mathrm{HCO_3^-}]$ in response to the decrease in $P_{\mathrm{CO_2}}$ are responsible for the general malaise that many people experience at high altitudes. If their blood pH does not adjust rapidly, the condition can develop into the life-threatening phenomenon known as altitude sickness.

A Video Summary of the pH Curve for a Strong Acid/Strong Base Titration:

Summary of the pH Curve for a Strong Acid/Strong Base Titration(opens in new window) [youtu.be]

Summary

Buffers are solutions that resist a change in pH after adding an acid or a base. Buffers contain a weak acid (HA) and its conjugate weak base (A^{-}). Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium shifts the equilibrium in such a way as to reduce the concentration of the common ion. The shift in equilibrium is called the common ion effect. Buffers are characterized by their pH range and buffer capacity. The useful pH range of a buffer depends strongly on the chemical properties of the conjugate weak acid–base pair used to prepare the buffer (the K_a or K_b), whereas its buffer capacity depends solely on the concentrations of the species in the solution. The pH of a buffer can be calculated using the Henderson-Hasselbalch approximation, which is valid for solutions whose concentrations are at least 100 times greater than their K_a values. Because no single buffer system can effectively maintain a constant pH value over the physiological range of approximately 5 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

15.6: Acid-Base Titration Curves

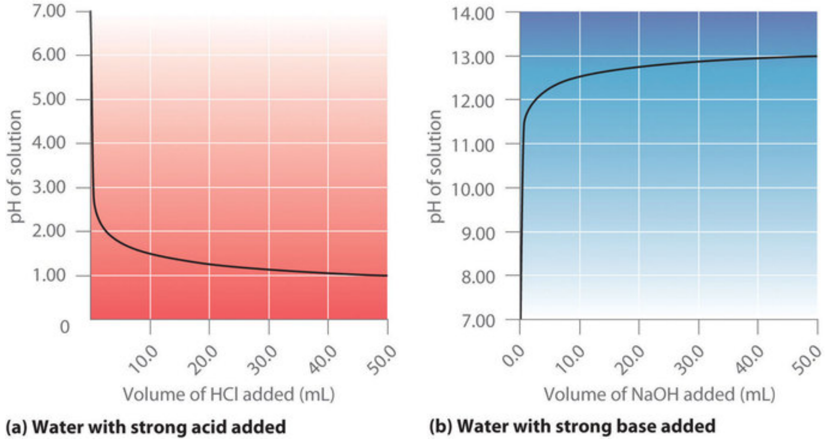
Learning Objectives

- To calculate the pH at any point in an acid–base titration.

In an acid–base titration, a buret is used to deliver measured volumes of an acid or a base solution of known concentration (the titrant) to a flask that contains a solution of a base or an acid, respectively, of unknown concentration (the unknown). If the concentration of the titrant is known, then the concentration of the unknown can be determined. The following discussion focuses on the pH changes that occur during an acid–base titration. Plotting the pH of the solution in the flask against the amount of acid or base added produces a titration curve. The shape of the curve provides important information about what is occurring in solution during the titration.

Titrations of Strong Acids and Bases

Figure $15.6.1a$ shows a plot of the pH as 0.20 M HCl is gradually added to 50.00 mL of pure water. The pH of the sample in the flask is initially 7.00 (as expected for pure water), but it drops very rapidly as HCl is added. Eventually the pH becomes constant at 0.70—a point well beyond its value of 1.00 with the addition of 50.0 mL of HCl (0.70 is the pH of 0.20 M HCl). In contrast, when 0.20 M NaOH is added to 50.00 mL of distilled water, the pH (initially 7.00) climbs very rapidly at first but then more gradually, eventually approaching a limit of 13.30 (the pH of 0.20 M NaOH), again well beyond its value of 13.00 with the addition of 50.0 mL of NaOH as shown in Figure $15.6.1b$ As you can see from these plots, the titration curve for adding a base is the mirror image of the curve for adding an acid.



(a) Water with strong acid added **(b) Water with strong base added**

Figure 15.6.1: Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water. (a) When 0.20 M HCl is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 M HCl. (b) Conversely, when 0.20 M NaOH is added to 50.0 mL of distilled water, the pH rapidly increases until it reaches a maximum at the pH of 0.20 M $NaOH$. (CC BY-SA-NC; Anonymous by request)

The graphs of water with strong acid added and water with strong base added are inverses of each other.

Suppose that we now add 0.20 M NaOH to 50.0 mL of a 0.10 M solution of HCl. Because HCl is a strong acid that is completely ionized in water, the initial $[H^+]$ is 0.10 M, and the initial pH is 1.00. Adding NaOH decreases the concentration of H+ because of the neutralization reaction (Figure $15.6.2a$):

$$\mathrm{OH^- + H^+ \rightleftharpoons H_2O}.$$

Thus the pH of the solution increases gradually. Near the equivalence point, however, the point at which the number of moles of base (or acid) added equals the number of moles of acid (or base) originally present in the solution, the pH increases much more rapidly because most of the $\mathrm{H^+}$ ions originally present have been consumed. For the titration of a monoprotic strong acid (HCl) with a monobasic strong base (NaOH), we can calculate the volume of base needed to reach the equivalence point from the following relationship:

$$moles\ of\ base = (volume)_b(molarity)_b V_b M_b = moles\ of\ acid = (volume)_a(molarity)_a = V_a M_a \tag{15.6.1}$$

If 0.20 M NaOH is added to 50.0 mL of a 0.10 M solution of HCl, we solve for V_b:

$$V_b(0.20Me) = 0.025L = 25mL$$

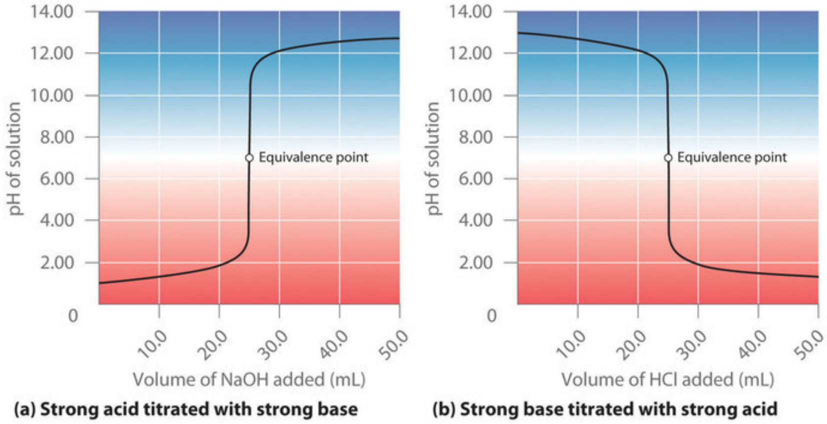


Figure 15.6.2: The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid(a) As 0.20 M NaOH is slowly added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases slowly once more. (b) Conversely, as 0.20 M HCl is slowly added to 50.0 mL of 0.10 M $NaOH$, the pH decreases slowly at first, then decreases very rapidly as the equivalence point is approached, and finally decreases slowly once more. (CC BY-SA-NC; Anonymous by request)

The titration curves of strong acid titrated with strong base and strong base titrated with strong acid are inverses of each other.

At the equivalence point (when 25.0 mL of $NaOH$ solution has been added), the neutralization is complete: only a salt remains in solution (NaCl), and the pH of the solution is 7.00. Adding more $NaOH$ produces a rapid increase in pH, but eventually the pH levels off at a value of about 13.30, the pH of 0.20 M $NaOH$.

As shown in Figure $15.6.2b$, the titration of 50.0 mL of a 0.10 M solution of $NaOH$ with 0.20 M HCl produces a titration curve that is nearly the mirror image of the titration curve in Figure $15.6.2a$. The pH is initially 13.00, and it slowly decreases as HCl is added. As the equivalence point is approached, the pH drops rapidly before leveling off at a value of about 0.70, the pH of 0.20 M HCl.

The titration of either a strong acid with a strong base or a strong base with a strong acid produces an S-shaped curve. The curve is somewhat asymmetrical because the steady increase in the volume of the solution during the titration causes the solution to become more dilute. Due to the leveling effect, the shape of the curve for a titration involving a strong acid and a strong base depends on only the concentrations of the acid and base, not their identities.

> The shape of the titration curve involving a strong acid and a strong base depends only on their concentrations, not their identities.

✓ Example 15.6.1: Hydrochloric Acid

Calculate the pH of the solution after 24.90 mL of 0.200 M $NaOH$ has been added to 50.00 mL of 0.100 M HCl.

Given: volumes and concentrations of strong base and acid

Asked for: pH

Strategy:

A. Calculate the number of millimoles of H^+ and OH^- to determine which, if either, is in excess after the neutralization reaction has occurred. If one species is in excess, calculate the amount that remains after the neutralization reaction.
B. Determine the final volume of the solution. Calculate the concentration of the species in excess and convert this value to pH.

Solution

A Because 0.100 mol/L is equivalent to 0.100 mmol/mL, the number of millimoles of H^+ in 50.00 mL of 0.100 M HCl can be calculated as follows:

$$50.00\ m\cancel{L} \left(\frac{0.100\ mmol\ HCl}{m\cancel{L}} \right) = 5.00\ mmol\ HCl = 5.00\ mmol\ H^+$$

The number of millimoles of NaOH added is as follows:

$$24.90\ m\cancel{L}\left(\frac{0.200\ mmol\ NaOH}{m\cancel{L}}\right)=4.98\ mmol\ NaOH=4.98\ mmol\ OH^-$$

Thus $\mathrm{H^+}$ is in excess. To completely neutralize the acid requires the addition of 5.00 mmol of $\mathrm{OH^-}$ to the HCl solution. Because only 4.98 mmol of OH^- has been added, the amount of excess $\mathrm{H^+}$ is 5.00 mmol − 4.98 mmol = 0.02 mmol of H^+.

B The final volume of the solution is 50.00 mL + 24.90 mL = 74.90 mL, so the final concentration of $\mathrm{H^+}$ is as follows:

$$\left[H^+\right]=\frac{0.02\ mmol\ H^+}{74.90\ mL}=3\times10^{-4}\ M$$

Hence,

$$pH\approx-\log[\mathrm{H^+}]=-\log(3\times10^{-4})=3.5$$

This is significantly less than the pH of 7.00 for a neutral solution.

? Exercise 15.6.1

Calculate the pH of a solution prepared by adding $40.00\ mL$ of $0.237\ M\ HCl$ to $75.00\ mL$ of a $0.133M$ solution of $NaOH$.

Answer

11.6

pH after the addition of 10 ml of Strong Base to a Strong Acid:

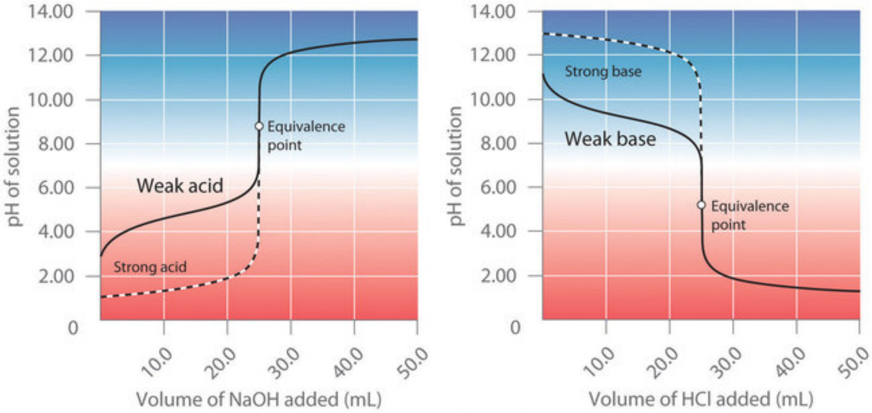
https://youtu.be/_cM1_-kdJ20 (opens in new window) pH at the Equivalence Point in a Strong Acid/Strong Base Titration:

https://youtu.be/7POGDA5Ql2M

Titrations of Weak Acids and Bases

In contrast to strong acids and bases, the shape of the titration curve for a weak acid or a weak base depends dramatically on the identity of the acid or the base and the corresponding K_a or K_b. As we shall see, the pH also changes much more gradually around the equivalence point in the titration of a weak acid or a weak base. As you learned previously, $[\mathrm{H^+}]$ of a solution of a weak acid (HA) is not equal to the concentration of the acid but depends on both its pK_a and its concentration. Because only a fraction of a weak acid dissociates, $[\backslash(\mathrm{H^+}]$ is less than $[\mathrm{HA}]$. Thus the pH of a solution of a weak acid is greater than the pH of a solution of a strong acid of the same concentration.

Figure $15.6.3a$ shows the titration curve for 50.0 mL of a 0.100 M solution of acetic acid with 0.200 M NaOH superimposed on the curve for the titration of 0.100 M HCl shown in part (a) in Figure $15.6.2$ Below the equivalence point, the two curves are very different. Before any base is added, the pH of the acetic acid solution is greater than the pH of the HCl solution, and the pH changes more rapidly during the first part of the titration. Note also that the pH of the acetic acid solution at the equivalence point is greater than 7.00. That is, at the equivalence point, the solution is basic. In addition, the change in pH around the equivalence point is only about half as large as for the HCl titration; the magnitude of the pH change at the equivalence point depends on the pK_a of the acid being titrated. Above the equivalence point, however, the two curves are identical. Once the acid has been neutralized, the pH of the solution is controlled only by the amount of excess NaOH present, regardless of whether the acid is weak or strong.



(a) Weak acid titrated with strong base **(b) Weak base titrated with strong acid**

Figure 15.6.3: The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid. (a) As 0.200 M NaOH is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH is shown as a dashed line. (b) As 0.200 M HCl is slowly added to 50.0 mL of 0.100 M NH3, the pH decreases slowly at first, then decreases rapidly as the equivalence point is approached, and then again decreases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M NaOH with 0.200 M HCl is shown as a dashed line. (CC BY-SA-NC; Anonymous by request)

The titration curves of weak acid titrated with strong base and weak base titrated with strong acid are inverse of each other. These curves are shorter than the titration curves with strong acid and strong base.

> The shape of the titration curve of a weak acid or weak base depends heavily on their identities and the K_a or K_b.

The titration curve in Figure $15.6.3a$ was created by calculating the starting pH of the acetic acid solution before any NaOH is added and then calculating the pH of the solution after adding increasing volumes of $NaOH$. The procedure is illustrated in the following subsection and Example $15.6.2$ for three points on the titration curve, using the pK_a of acetic acid (4.76 at 25°C; $K_a = 1.7 \times 10^{-5}$.

Calculating the pH of a Solution of a Weak Acid or a Weak Base

As explained discussed, if we know K_a or K_b and the initial concentration of a weak acid or a weak base, we can calculate the pH of a solution of a weak acid or a weak base by setting up a ICE table (i.e, initial concentrations, changes in concentrations, and final concentrations). In this situation, the initial concentration of acetic acid is 0.100 M. If we define x as $[\mathrm{H^+}]$ due to the dissociation of the acid, then the table of concentrations for the ionization of 0.100 M acetic acid is as follows:

$$\mathrm{CH_3CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CO_2^-}$$

table of concentrations for the ionization of 0.100 M acetic acid

ICE	$[CH_3CO_2H]$	$[H^+]$	$[CH_3CO_2^-]$
initial	0.100	1.00×10^{-7}	0
change	−x	+x	+x
final	0.100 − x	x	x

In this and all subsequent examples, we will ignore $[H^+]$ and $[OH^-]$ due to the autoionization of water when calculating the final concentration. However, you should use Equation 16.45 and Equation 16.46 to check that this assumption is justified.

Inserting the expressions for the final concentrations into the equilibrium equation (and using approximations),

$$\begin{aligned} K_a &= \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} \\ &= \frac{(x)(x)}{0.100 - x} \\ &\approx \frac{x^2}{0.100} \\ &\approx 1.74 \times 10^{-5} \end{aligned}$$

Solving this equation gives $x = [H^+] = 1.32 \times 10^{-3}\ M$. Thus the pH of a 0.100 M solution of acetic acid is as follows:

$$pH = -\log(1.32 \times 10^{-3}) = 2.879$$

pH at the Start of a Weak Acid/Strong Base Titration: https://youtu.be/AtdBKfrfJNg

Calculating the pH during the Titration of a Weak Acid or a Weak Base

Now consider what happens when we add 5.00 mL of 0.200 M NaOH to 50.00 mL of 0.100 M CH_3CO_2H (part (a) in Figure $15.6.3$). Because the neutralization reaction proceeds to completion, all of the OH^- ions added will react with the acetic acid to generate acetate ion and water:

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightarrow CH_3CO^-_{2\ (aq)} + H_2O_{(l)} \tag{15.6.2}$$

All problems of this type must be solved in two steps: a stoichiometric calculation followed by an equilibrium calculation. In the first step, we use the stoichiometry of the neutralization reaction to calculate the amounts of acid and conjugate base present in solution after the neutralization reaction has occurred. In the second step, we use the equilibrium equation to determine $[\mathrm{H^+}]$ of the resulting solution.

Step 1

To determine the amount of acid and conjugate base in solution after the neutralization reaction, we calculate the amount of $\mathrm{CH_3CO_2H}$ in the original solution and the amount of $\mathrm{OH^-}$ in the NaOH solution that was added. The acetic acid solution contained

$$50.00\ \cancel{mL} (0.100\ mmol (\mathrm{CH_3CO_2H})/\ \cancel{mL}) = 5.00\ mmol (\mathrm{CH_3CO_2H})$$

The NaOH solution contained

$$5.00\text{ mL=1.00 mmol } NaOH$$

Comparing the amounts shows that CH_3CO_2H is in excess. Because OH^- reacts with CH_3CO_2H in a 1:1 stoichiometry, the amount of excess CH_3CO_2H is as follows:

$$5.00 \text{ mmol } CH_3CO_2H - 1.00 \text{ mmol } OH^- = 4.00 \text{ mmol } CH_3CO_2H$$

Each 1 mmol of OH^- reacts to produce 1 mmol of acetate ion, so the final amount of $CH_3CO_2^-$ is 1.00 mmol.

The stoichiometry of the reaction is summarized in the following ICE table, which shows the numbers of moles of the various species, not their concentrations.

$$CH_3CO_2H(aq) + OH^-(aq) \rightleftharpoons CH_3CO_2^-(aq) + H_2O(l)$$

ICE table

ICE	$[CH_3CO_2H]$	$[OH^-]$	$[CH_3CO_2^-]$
initial	5.00 mmol	1.00 mmol	0 mmol
change	−1.00 mmol	−1.00 mmol	+1.00 mmol
final	4.00 mmol	0 mmol	1.00 mmol

This ICE table gives the initial amount of acetate and the final amount of OH^- ions as 0. Because an aqueous solution of acetic acid always contains at least a small amount of acetate ion in equilibrium with acetic acid, however, the initial acetate concentration is not actually 0. The value can be ignored in this calculation because the amount of $CH_3CO_2^-$ in equilibrium is insignificant compared to the amount of OH^- added. Moreover, due to the autoionization of water, no aqueous solution can contain 0 mmol of OH^-, but the amount of OH^- due to the autoionization of water is insignificant compared to the amount of OH^- added. We use the initial amounts of the reactants to determine the stoichiometry of the reaction and defer a consideration of the equilibrium until the second half of the problem.

Step 2

To calculate $[H^+]$ at equilibrium following the addition of $NaOH$, we must first calculate $[CH_3CO_2H]$ and $[CH_3CO_2^-]$ using the number of millimoles of each and the total volume of the solution at this point in the titration:

$$final\ volume = 50.00\ mL + 5.00\ mL = 55.00\ mL$$

$$[CH_3CO_2H] = \frac{4.00\ mmol\ CH_3CO_2H}{55.00\ mL} = 7.27 \times 10^{-2}\ M$$

$$\left[CH_3CO_2^-\right] = \frac{1.00\ mmol\ CH_3CO_2^-}{55.00\ mL} = 1.82 \times 10^{-2}\ M$$

Knowing the concentrations of acetic acid and acetate ion at equilibrium and K_a for acetic acid (1.74×10^{-5}), we can calculate $[H^+]$ at equilibrium:

$$K_a = \frac{\left[CH_3CO_2^-\right][H^+]}{[CH_3CO_2H]}$$

$$[H^+] = \frac{K_a[CH_3CO_2H]}{\left[CH_3CO_2^-\right]} = \frac{(1.72 \times 10^{-5})(7.27 \times 10^{-2}\ M)}{(1.82 \times 10^{-2})} = 6.95 \times 10^{-5}\ M$$

Calculating $-\log[H^+]$ gives

$$pH = -\log(6.95 \times 10^{-5}) = 4.158.$$

Comparing the titration curves for HCl and acetic acid in Figure $15.6.3a$, we see that adding the same amount (5.00 mL) of 0.200 M NaOH to 50 mL of a 0.100 M solution of both acids causes a much smaller pH change for HCl (from 1.00 to 1.14) than for acetic acid (2.88 to 4.16). This is consistent with the qualitative description of the shapes of the titration curves at the beginning of this section. In Example $15.6.2$, we calculate another point for constructing the titration curve of acetic acid.

pH Before the Equivalence Point of a Weak Acid/Strong Base Titration:

https://youtu.be/znpwGCsefXc

Example 15.6.2

What is the pH of the solution after 25.00 mL of 0.200 M NaOH is added to 50.00 mL of 0.100 M acetic acid?

Given: volume and molarity of base and acid

Asked for: pH

Strategy:

A. Write the balanced chemical equation for the reaction. Then calculate the initial numbers of millimoles of OH^- and CH_3CO_2H. Determine which species, if either, is present in excess.
B. Tabulate the results showing initial numbers, changes, and final numbers of millimoles.
C. If excess acetate is present after the reaction with $\mathrm{OH^-}$, write the equation for the reaction of acetate with water. Use a tabular format to obtain the concentrations of all the species present.
D. Calculate K_b using the relationship $K_w = K_a K_b$. Calculate [OH−] and use this to calculate the pH of the solution.

Solution

A Ignoring the spectator ion (Na^+), the equation for this reaction is as follows:

$$CH_3CO_2H_{(aq)} + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l)$$

The initial numbers of millimoles of OH^- and CH_3CO_2H are as follows:

$$25.00\text{ mL}(0.200\text{ mmol OH}{-}\text{mL}=5.00\text{ mmol } OH-$$

$$50.00\ mL(0.100 CH_3CO_2HL = 5.00 mmol\ CH_3CO_2H$$

The number of millimoles of OH^- equals the number of millimoles of CH_3CO_2H, so neither species is present in excess.

B Because the number of millimoles of OH^- added corresponds to the number of millimoles of acetic acid in solution, this is the equivalence point. The results of the neutralization reaction can be summarized in tabular form.

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3CO_2^-(aq) + H_2O(l)$$

results of the neutralization reaction

ICE	$[\mathrm{CH_3CO_2H}]$	$[\mathrm{OH^-}]$	$[\mathrm{CH_3CO_2^-}]$
initial	5.00 mmol	5.00 mmol	0 mmol
change	−5.00 mmol	−5.00 mmol	+5.00 mmol
final	0 mmol	0 mmol	5.00 mmol

C Because the product of the neutralization reaction is a weak base, we must consider the reaction of the weak base with water to calculate [H+] at equilibrium and thus the final pH of the solution. The initial concentration of acetate is obtained from the neutralization reaction:

$$[\mathrm{CH_3CO_2}] = \frac{5.00\ mmol\ CH_3CO_2^-}{(50.00+25.00)\ mL} = 6.67\times10^{-2}\ M$$

The equilibrium reaction of acetate with water is as follows:

$$\mathrm{CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)}$$

The equilibrium constant for this reaction is

$$K_b = \frac{K_w}{K_a} \tag{15.6.3}$$

where K_a is the acid ionization constant of acetic acid. We therefore define x as $[\mathrm{OH^-}]$ produced by the reaction of acetate with water. Here is the completed table of concentrations:

$$H_2O_{(l)} + CH_3CO^-_{2(aq)} \rightleftharpoons CH_3CO_2H_{(aq)} + OH^-_{(aq)}$$

completed table of concentrations

	$[\mathrm{CH_3CO_2^-}]$	$[\mathrm{CH_3CO_2H}]$	$[\mathrm{OH^-}]$
initial	0.0667	0	1.00 × 10−7
change	−x	+x	+x
final	(0.0667 − x)	x	x

D We can obtain K_b by substituting the known values into Equation 15.6.3:

$$K_b = \frac{K_w}{K_a} = \frac{1.01\times10^{-14}}{1.74\times10^{-5}} = 5.80\times10^{-10} \tag{15.6.4}$$

Substituting the expressions for the final values from the ICE table into Equation 15.6.4 and solving for x:

$$\begin{aligned} \frac{x^2}{0.0667} &= 5.80\times10^{-10} \\ x &= \sqrt{(5.80\times10^{-10})(0.0667)} \\ &= 6.22\times10^{-6} \end{aligned}$$

Thus $[OH^-] = 6.22\times10^{-6}\ M$ and the pH of the final solution is 8.794 (Figure $15.6.3a$). As expected for the titration of a weak acid, the pH at the equivalence point is greater than 7.00 because the product of the titration is a base, the acetate ion, which then reacts with water to produce $\mathrm{OH^-}$.

❓ Exercise 15.6.2

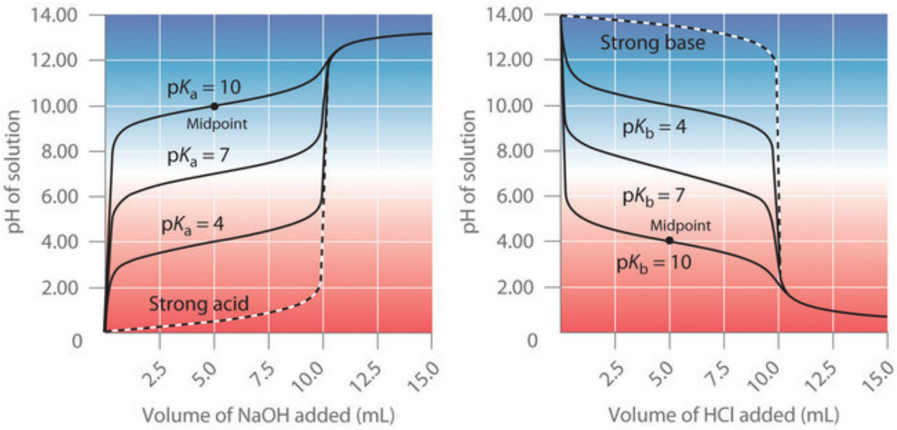
Calculate the pH of a solution prepared by adding 45.0 mL of a 0.213 M HCl solution to 125.0 mL of a 0.150 M solution of ammonia. The pK_b of ammonia is 4.75 at 25°C.

Answer

9.23

As shown in part (b) in Figure 15.6.3, the titration curve for NH3, a weak base, is the reverse of the titration curve for acetic acid. In particular, the pH at the equivalence point in the titration of a weak base is less than 7.00 because the titration produces an acid.

The identity of the weak acid or weak base being titrated strongly affects the shape of the titration curve. Figure 15.6.4 illustrates the shape of titration curves as a function of the pK_a or the pK_b. As the acid or the base being titrated becomes weaker (its pK_a or pK_b becomes larger), the pH change around the equivalence point decreases significantly. With very dilute solutions, the curve becomes so shallow that it can no longer be used to determine the equivalence point.



(a) Weak acids titrated with strong base **(b) Weak bases titrated with strong acid**

Figure 15.6.4: Effect of Acid or Base Strength on the Shape of Titration Curves. Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the pK_a or pK_b of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M NaOH added to 10.00 mL of 1.00 M solutions of weak acids with the indicated pK_a values. (b) Solution pH as a function of the volume of 1.00 M HCl added to 10.00 mL of 1.00 M solutions of weak bases with the indicated pK_b values. The shapes of the two sets of curves are essentially identical, but one is flipped vertically in relation to the other. Midpoints are indicated for the titration curves corresponding to pK_a = 10 and pK_b = 10. (CC BY-SA-NC; Anonymous by request)

The titration curves of weak acids with strong base and weak bases titrated with strong acid are inverses of each other. Three weak acids and three weak bases with pKa and pKb of 4, 7, and 10 are used.

One point in the titration of a weak acid or a weak base is particularly important: the midpoint of a titration is defined as the point at which exactly enough acid (or base) has been added to neutralize one-half of the acid (or the base) originally present and occurs halfway to the equivalence point. The midpoint is indicated in Figures 15.6.4a and 15.6.4b for the two shallowest curves. By definition, at the midpoint of the titration of an acid, [HA] = [A−]. Recall that the ionization constant for a weak acid is as follows:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

If $[HA] = [A^-]$, this reduces to $K_a = [H_3O^+]$. Taking the negative logarithm of both sides,

$$-\log K_a = -\log[H_3O+]$$

From the definitions of pK_a and pH, we see that this is identical to

$$pK_a = pH \tag{15.6.5}$$

Thus the pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid, as indicated in part (a) in Figure 15.6.4 for the weakest acid where we see that the midpoint for pK_a = 10 occurs at pH = 10. Titration methods can therefore be used to determine both the concentration and the pK_a (or the pK_b) of a weak acid (or a weak base).

> The pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid.

Titrations of Polyprotic Acids or Bases

When a strong base is added to a solution of a polyprotic acid, the neutralization reaction occurs in stages. The most acidic group is titrated first, followed by the next most acidic, and so forth. If the pK_a values are separated by at least three pK_a units, then the overall titration curve shows well-resolved "steps" corresponding to the titration of each proton. A titration of the triprotic acid H_3PO_4 with NaOH is illustrated in Figure 15.6.5 and shows two well-defined steps: the first midpoint corresponds to pK_a1, and the second midpoint corresponds to pK_{a2}. Because HPO_4^{2-} is such a weak acid, pK_{a3} has such a high value that the third step cannot be resolved using 0.100 M NaOH as the titrant.

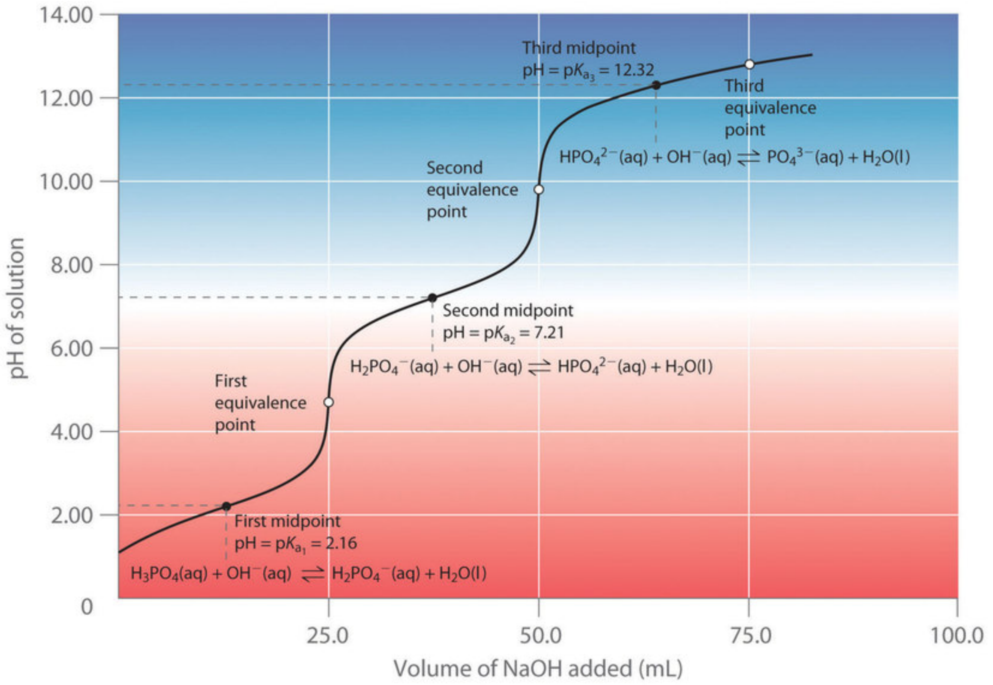
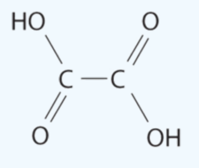


Figure 15.6.5: Titration Curve for Phosphoric Acid (H_3PO_4, a Typical Polyprotic Acid. The curve for the titration of 25.0 mL of a 0.100 M H_3PO_4 solution with 0.100 M NaOH along with the species in solution at each Ka is shown. Note the two distinct equivalence points corresponding to deprotonation of H_3PO_4 at pH ≈ 4.6 and $H_2PO_4^{2-}$ at pH ≈ 9.8. Because HPO_4^{2-} is a very weak acid, the third equivalence point, at pH ≈ 13, is not well defined. (CC BY-SA-NC; Anonymous by request)

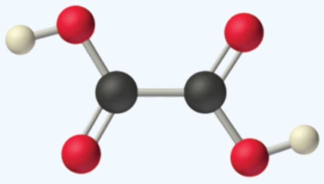
The titration curve for the reaction of a polyprotic base with a strong acid is the mirror image of the curve shown in Figure 15.6.5. The initial pH is high, but as acid is added, the pH decreases in steps if the successive pK_b values are well separated. Table E1 lists the ionization constants and pK_a values for some common polyprotic acids and bases.

✓ Example 15.6.3

Calculate the pH of a solution prepared by adding 55.0 mL of a 0.120 M NaOH solution to 100.0 mL of a 0.0510 M solution of oxalic acid ($\mathrm{HO_2CCO_2H}$), a diprotic acid (abbreviated as $\mathrm{H_2ox}$). Oxalic acid, the simplest dicarboxylic acid, is found in rhubarb and many other plants. Rhubarb leaves are toxic because they contain the calcium salt of the fully deprotonated form of oxalic acid, the oxalate ion ($\mathrm{O_2CCO_2^{2-}}$, abbreviated $\mathrm{ox^{2-}}$).Oxalate salts are toxic for two reasons. First, oxalate salts of divalent cations such as $\mathrm{Ca^{2+}}$ are insoluble at neutral pH but soluble at low pH. As a result, calcium oxalate dissolves in the dilute acid of the stomach, allowing oxalate to be absorbed and transported into cells, where it can react with calcium to form tiny calcium oxalate crystals that damage tissues. Second, oxalate forms stable complexes with metal ions, which can alter the distribution of metal ions in biological fluids.



oxalic acid



Given: volume and concentration of acid and base

Asked for: pH

Strategy:

A. Calculate the initial millimoles of the acid and the base. Use a tabular format to determine the amounts of all the species in solution.
B. Calculate the concentrations of all the species in the final solution. Determine $[\mathrm{H+}]$ and convert this value to pH.

Solution:

A Table E5 gives the pK_a values of oxalic acid as 1.25 and 3.81. Again we proceed by determining the millimoles of acid and base initially present:

$$100.00\ \cancel{mL}\left(\frac{0.510\ mmol\ H_2ox}{\cancel{mL}}\right)=5.10\ mmol\ H_2ox$$

$$55.00\ \cancel{mL}\left(\frac{0.120\ mmol\ NaOH}{\cancel{mL}}\right)=6.60\ mmol\ NaOH$$

The strongest acid (H_2ox) reacts with the base first. This leaves (6.60 − 5.10) = 1.50 mmol of OH^- to react with Hox−, forming ox^{2-} and H_2O. The reactions can be written as follows:

$$\underset{5.10\ mmol}{H_2ox}+\underset{6.60\ mmol}{OH^-}\rightarrow\underset{5.10\ mmol}{Hox^-}+\underset{5.10\ mmol}{H_2O}$$

$$\underset{5.10\ mmol}{Hox^-}+\underset{1.50\ mmol}{OH^-}\rightarrow\underset{1.50\ mmol}{ox^{2-}}+\underset{1.50\ mmol}{H_2O}$$

In tabular form,

Solutions to Example 17.3.3

	H_2ox	OH^-	Hox^-	ox^{2-}
initial	5.10 mmol	6.60 mmol	0 mmol	0 mmol
change (step 1)	−5.10 mmol	−5.10 mmol	+5.10 mmol	0 mmol
final (step 1)	0 mmol	1.50 mmol	5.10 mmol	0 mmol
change (step 2)	—	−1.50 mmol	−1.50 mmol	+1.50 mmol
final	0 mmol	0 mmol	3.60 mmol	1.50 mmol

B The equilibrium between the weak acid (Hox^-) and its conjugate base (ox^{2-}) in the final solution is determined by the magnitude of the second ionization constant, $K_{a2}=10^{-3.81}=1.6\times10^{-4}$. To calculate the pH of the solution, we need to know $[H^+]$, which is determined using exactly the same method as in the acetic acid titration in Example $15.6.2$:

$$\text{final volume of solution}=100.0\,mL+55.0\,mL=155.0\,mL$$

Thus the concentrations of Hox^- and ox^{2-} are as follows:

$$\left[Hox^-\right]=\frac{3.60\ mmol\ Hox^-}{155.0\ mL}=2.32\times10^{-2}\ M$$

$$\left[ox^{2-}\right]=\frac{1.50\ mmol\ ox^{2-}}{155.0\ mL}=9.68\times10^{-3}\ M$$

We can now calculate [H+] at equilibrium using the following equation:

$$K_{a2}=\frac{\left[ox^{2-}\right]\left[H^+\right]}{\left[Hox^-\right]}$$

Rearranging this equation and substituting the values for the concentrations of Hox^- and ox^{2-},

$$\left[H^+\right]=\frac{K_{a2}\left[Hox^-\right]}{\left[ox^{2-}\right]}=\frac{\left(1.6\times10^{-4}\right)\left(2.32\times10^{-2}\right)}{\left(9.68\times10^{-3}\right)}=3.7\times10^{-4}\ M$$

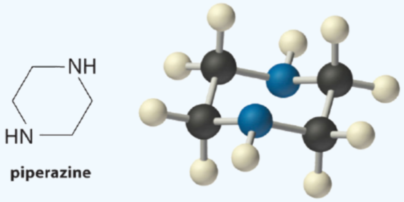
So

$$pH=-\log\left[H^+\right]=-\log\left(3.7\times10^{-4}\right)=3.43$$

This answer makes chemical sense because the pH is between the first and second pK_a values of oxalic acid, as it must be. We added enough hydroxide ion to completely titrate the first, more acidic proton (which should give us a pH greater than pK_{a1}), but we added only enough to titrate less than half of the second, less acidic proton, with pK_{a2}. If we had added exactly enough hydroxide to completely titrate the first proton plus half of the second, we would be at the midpoint of the second step in the titration, and the pH would be 3.81, equal to pK_{a2}.

Exercise 15.6.3: Piperazine

Piperazine is a diprotic base used to control intestinal parasites (“worms”) in pets and humans. A dog is given 500 mg (5.80 mmol) of piperazine (pK_{b1} = 4.27, pK_{b2} = 8.67). If the dog’s stomach initially contains 100 mL of 0.10 M HCl (pH = 1.00), calculate the pH of the stomach contents after ingestion of the piperazine.



Answer

pH=4.9

Indicators

In practice, most acid–base titrations are not monitored by recording the pH as a function of the amount of the strong acid or base solution used as the titrant. Instead, an acid–base indicator is often used that, if carefully selected, undergoes a dramatic color change at the pH corresponding to the equivalence point of the titration. Indicators are weak acids or bases that exhibit intense colors that vary with pH. The conjugate acid and conjugate base of a good indicator have very different colors so that they can be distinguished easily. Some indicators are colorless in the conjugate acid form but intensely colored when deprotonated (phenolphthalein, for example), which makes them particularly useful.

We can describe the chemistry of indicators by the following general equation:

$$\mathrm{HIn(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{In^-(aq)}$$

where the protonated form is designated by HIn and the conjugate base by $\mathrm{In^-}$. The ionization constant for the deprotonation of indicator HIn is as follows:

$$K_{In} = \frac{[\mathrm{H^+}][\mathrm{In^-}]}{[\mathrm{HIn}]} \tag{15.6.6}$$

The pK_{in} (its pK_a) determines the pH at which the indicator changes color.

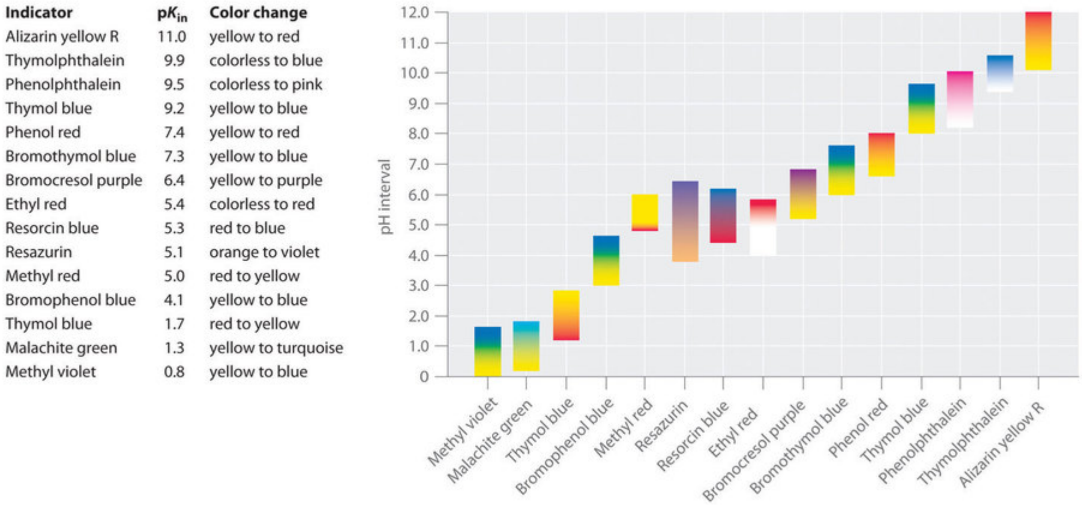
Many different substances can be used as indicators, depending on the particular reaction to be monitored. For example, red cabbage juice contains a mixture of colored substances that change from deep red at low pH to light blue at intermediate pH to yellow at high pH. Similarly, *Hydrangea macrophylla* flowers can be blue, red, pink, light purple, or dark purple depending on the soil pH (Figure $15.6.6$). Acidic soils will produce blue flowers, whereas alkaline soils will produce pinkish flowers.

Irrespective of the origins, a good indicator must have the following properties:

- The color change must be easily detected.
- The color change must be rapid.
- The indicator molecule must not react with the substance being titrated.
- To minimize errors, the indicator should have a pK_{in} that is within one pH unit of the expected pH at the equivalence point of the titration.

Figure 15.6.6: Naturally occurring pH indicators can be found in red cabbage and Hydrangea macrophylla flowers. Red Cabbage image (CC BY-SA 3.0; KENPEI via Wikipedia) and Hydrangea macrophylla flowers (pixabay).

Synthetic indicators have been developed that meet these criteria and cover virtually the entire pH range. Figure $15.6.7$ shows the approximate pH range over which some common indicators change color and their change in color. In addition, some indicators (such as thymol blue) are polyprotic acids or bases, which change color twice at widely separated pH values.



Indicator	pK_{in}	Color change
Alizarin yellow R	11.0	yellow to red
Thymolphthalein	9.9	colorless to blue
Phenolphthalein	9.5	colorless to pink
Thymol blue	9.2	yellow to blue
Phenol red	7.4	yellow to red
Bromothymol blue	7.3	yellow to blue
Bromocresol purple	6.4	yellow to purple
Ethyl red	5.4	colorless to red
Resorcin blue	5.3	red to blue
Resazurin	5.1	orange to violet
Methyl red	5.0	red to yellow
Bromophenol blue	4.1	yellow to blue
Thymol blue	1.7	red to yellow
Malachite green	1.3	yellow to turquoise
Methyl violet	0.8	yellow to blue

Figure 15.6.7: Some Common Acid–Base Indicators. Approximate colors are shown, along with pK_{in} values and the pH range over which the color changes. (CC BY-SA-NC; Anonymous by request)

It is important to be aware that an indicator does not change color abruptly at a particular pH value; instead, it actually undergoes a pH titration just like any other acid or base. As the concentration of HIn decreases and the concentration of In− increases, the color of the solution slowly changes from the characteristic color of HIn to that of In−. As we will see later, the [In−]/[HIn] ratio changes from 0.1 at a pH one unit below pKin to 10 at a pH one unit above pKin. Thus most indicators change color over a pH range of about two pH units.

We have stated that a good indicator should have a pKin value that is close to the expected pH at the equivalence point. For a strong acid–strong base titration, the choice of the indicator is not especially critical due to the very large change in pH that occurs around the equivalence point. In contrast, using the wrong indicator for a titration of a weak acid or a weak base can result in relatively large errors, as illustrated in Figure $15.6.8$ This figure shows plots of pH versus volume of base added for the titration of 50.0 mL of a 0.100 M solution of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M $NaOH$. The pH ranges over which two common indicators (methyl red, $pK_{in} = 5.0$, and phenolphthalein, $pK_{in} = 9.5$) change color are also shown. The horizontal bars indicate the pH ranges over which both indicators change color cross the HCl titration curve, where it is almost vertical. Hence both indicators change color when essentially the same volume of NaOH has been added (about 50 mL), which corresponds to the equivalence point. In contrast, the titration of acetic acid will give very different results depending on whether methyl red or phenolphthalein is used as the indicator. Although the pH range over which phenolphthalein changes color is slightly greater than the pH at the equivalence point of the strong acid titration, the error will be negligible due to the slope of this portion of the titration curve. Just as with the HCl titration, the phenolphthalein indicator will turn pink when about 50 mL of NaOH has been added to the acetic acid solution. In contrast, methyl red begins to change from red to yellow around pH 5, which is near the midpoint of the acetic acid titration, not the equivalence point. Adding only about 25–30 mL of NaOH will therefore cause the methyl red indicator to change color, resulting in a huge error.

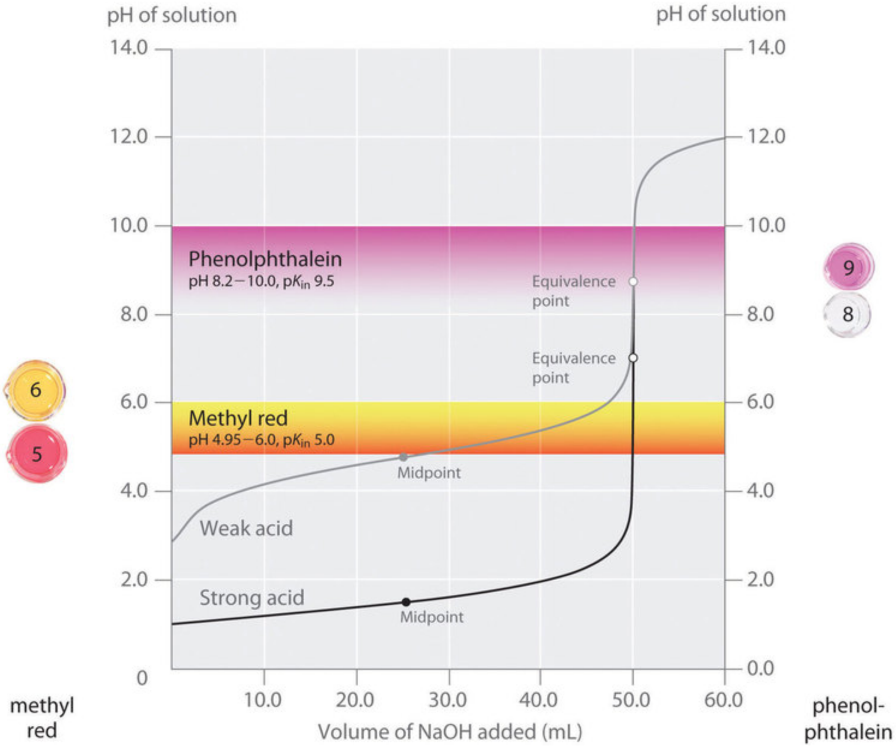


Figure 15.6.8: Choosing the Correct Indicator for an Acid–Base Titration. (CC BY-SA-NC; Anonymous by request)

If the pH of the solution is between 4.95 and 6 then methyl red should be used. If the pH is between 8,2 and 10 then phenolphthalein should be used.

The graph shows the results obtained using two indicators (methyl red and phenolphthalein) for the titration of 0.100 M solutions of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M $NaOH$. Due to the steepness of the titration curve of a strong acid around the equivalence point, either indicator will rapidly change color at the equivalence point for the titration of the strong acid. In contrast, the pKin for methyl red (5.0) is very close to the pK_a of acetic acid (4.76); the midpoint of the color change for methyl red occurs near the midpoint of the titration, rather than at the equivalence point.

In general, for titrations of strong acids with strong bases (and vice versa), any indicator with a pKin between about 4.0 and 10.0 will do. For the titration of a weak acid, however, the pH at the equivalence point is greater than 7.0, so an indicator such as phenolphthalein or thymol blue, with pKin > 7.0, should be used. Conversely, for the titration of a weak base, where the pH at the equivalence point is less than 7.0, an indicator such as methyl red or bromocresol blue, with pKin < 7.0, should be used.

The existence of many different indicators with different colors and pKin values also provides a convenient way to estimate the pH of a solution without using an expensive electronic pH meter and a fragile pH electrode. Paper or plastic strips impregnated with combinations of indicators are used as “pH paper,” which allows you to estimate the pH of a solution by simply dipping a piece of pH paper into it and comparing the resulting color with the standards printed on the container (Figure 15.6.9).

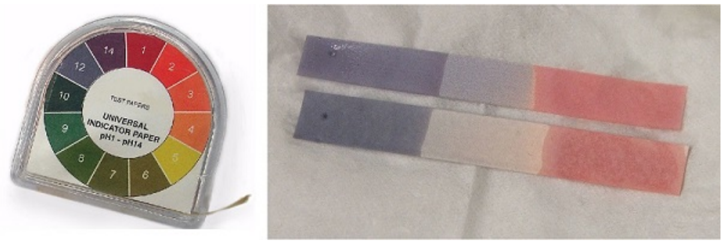


Figure 15.6.9: pH Paper. pH paper contains a set of indicators that change color at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the color to the standards provided. (CC BY-SA-NC; Anonymous by request)

pH Indicators: pH Indicators(opens in new window) [youtu.be]

Summary and Takeaway

Plots of acid–base titrations generate titration curves that can be used to calculate the pH, the pOH, the pK_a, and the pK_b of the system. The shape of a titration curve, a plot of pH versus the amount of acid or base added, provides important information about what is occurring in solution during a titration. The shapes of titration curves for weak acids and bases depend dramatically on the identity of the compound. The equivalence point of an acid–base titration is the point at which exactly enough acid or base has been added to react completely with the other component. The equivalence point in the titration of a strong acid or a strong base occurs at pH 7.0. In titrations of weak acids or weak bases, however, the pH at the equivalence point is greater or less than 7.0, respectively. The pH tends to change more slowly before the equivalence point is reached in titrations of weak acids and weak bases than in titrations of strong acids and strong bases. The pH at the midpoint, the point halfway on the titration curve to the equivalence point, is equal to the pK_a of the weak acid or the pK_b of the weak base. Thus titration methods can be used to determine both the concentration and the pK_a (or the pK_b) of a weak acid (or a weak base). Acid–base indicators are compounds that change color at a particular pH. They are typically weak acids or bases whose changes in color correspond to deprotonation or protonation of the indicator itself.

15.7: Polyprotic Acids

Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

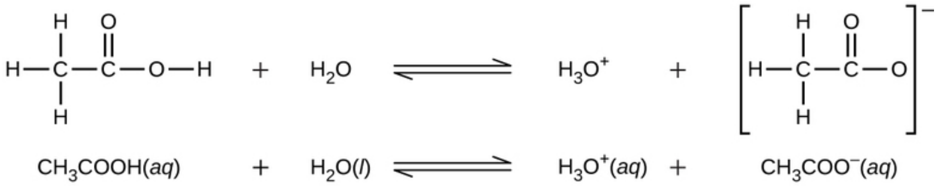
We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, $\mathrm{HNO_3}$, and HCN that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:

$$\mathrm{HCl}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{Cl^-}(aq)$$

$$\mathrm{HNO_3}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{NO_3^-}(aq)$$

$$\mathrm{HCN}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{CN^-}(aq)$$

Even though it contains four hydrogen atoms, acetic acid, $\mathrm{CH_3CO_2H}$, is also monoprotic because only the hydrogen atom from the carboxyl group ($-\mathrm{COOH}$) reacts with bases:



This image contains two equilibrium reactions. The first shows a C atom bonded to three H atoms and another C atom. The second C atom is double bonded to an O atom and also forms a single bond to another O atom. The second O atom is bonded to an H atom. There is a plus sign and then the molecular formula H subscript 2 O. An equilibrium arrow follows the H subscript 2 O. To the right of the arrow is H subscript 3 O superscript positive sign. There is a plus sign. The final structure shows a C atom bonded the three H atoms and another C atom. This second C atom is double bonded to an O atom and single bonded to another O atom. The entire structure is in brackets and a superscript negative sign appears outside the brackets. The second reaction shows C H subscript 3 C O O H (a q) plus H subscript 2 O (l) equilibrium arrow H subscript 3 O (a q) plus C H subscript 3 C O O superscript negative sign (a q).

Similarly, monoprotic bases are bases that will accept a single proton.

Diprotic Acids

Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

- **The first ionization is**

$$\mathrm{H_2SO_4}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HSO_4^-}(aq)$$

with $K_{\mathrm{a1}} > 10^2;\ complete\ dissociation$.

- **The second ionization is**

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq)$$

with $K_{\mathrm{a2}} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids. When we make a solution of a weak diprotic acid, we get a solution that contains a mixture of acids. Carbonic acid, $\mathrm{H_2CO_3}$, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

- **First Ionization**

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq)$$

with

$$K_{\mathrm{H_2CO_3}} = \frac{[\mathrm{H_3O^+}][\mathrm{HCO_3^-}]}{[\mathrm{H_2CO_3}]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

- **Second Ionization**

$$\mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CO_3^{2-}}(aq)$$

with

$$K_{\mathrm{HCO_3^-}} = \frac{[\mathrm{H_3O^+}][\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]} = 4.7 \times 10^{-11}$$

$K_{\mathrm{H_2CO_3}}$ is larger than $K_{\mathrm{HCO_3^-}}$ by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that little of the $\mathrm{HCO_3^-}$ formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and $\mathrm{HCO_3^-}$ are practically equal in a pure aqueous solution of H_2CO_3.

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This can simplify our work considerably because we can determine the concentration of H_3O^+ and the conjugate base from the first ionization, then determine the concentration of the conjugate base of the second ionization in a solution with concentrations determined by the first ionization.

Example 15.7.1: Ionization of a Diprotic Acid

When we buy soda water (carbonated water), we are buying a solution of carbon dioxide in water. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are $[\mathrm{H_3O^+}]$, $[\mathrm{HCO_3^-}]$, and $[\mathrm{CO_3^{2-}}]$ in a saturated solution of CO_2 with an initial $[H_2CO_3]$ = 0.033 *M*?

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \quad K_{a1} = 4.3 \times 10^{-7} \qquad \text{(equilibrium step 1)}$$

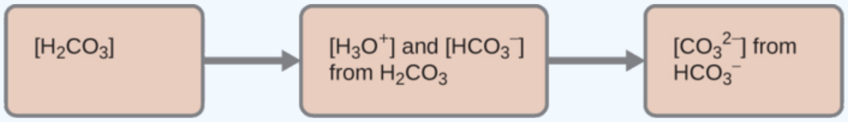
$$\mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CO_3^{2-}}(aq) \quad K_{a2} = 4.7 \times 10^{-11} \qquad \text{(equilibrium step 2)}$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than $\mathrm{HCO_3^-}$, so $\mathrm{H_2CO_3}$ is the dominant producer of hydronium ion in solution. Thus there are two parts in the solution of this problem:

1. Using the customary four steps, we determine the concentration of H_3O^+ and $\mathrm{HCO_3^-}$ produced by ionization of H_2CO_3.
2. Then we determine the concentration of $\mathrm{CO_3^{2-}}$ in a solution with the concentration of H_3O^+ and $\mathrm{HCO_3^-}$ determined in (1).

To summarize:



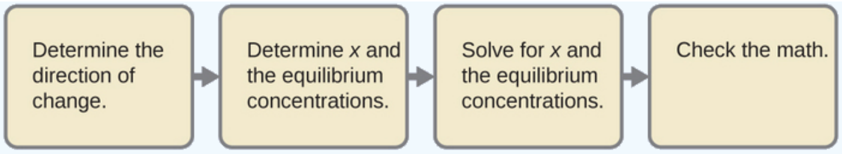
Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “left bracket H subscript 2 C O subscript 3 right bracket.” The second is labeled “left bracket H subscript 3 O superscript plus right bracket and left bracket H C O subscript 3 superscript negative right bracket from H subscript 2 C O subscript 3.” The third is labeled “left bracket C O subscript 3 superscript 2 negative right bracket from H C O subscript 3 superscript negative.”

1. First Ionization: Determine the concentrations of $\mathrm{H_3O^+}$ *and* $\mathrm{HCO_3^-}$.

Since equilibrium step 1 is has a much bigger $K_{a1} = 4.3 \times 10^{-7}$ than $K_{a2} = 4.7 \times 10^{-11}$ for equilibrium step 2, we can safely ignore the second ionization step and focus only on the first step (but address it in next part of problem).

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \quad K_{a1} = 4.3 \times 10^{-7}$$

As for the ionization of any other weak acid:



Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “Determine the direction of change.” The second is labeled “Determine x and the equilibrium concentrations.” The third is labeled “Solve for x and the equilibrium concentrations.” The fourth is labeled “Check the math.”

An abbreviated table of changes and concentrations shows:

Abbreviated table of changes and concentrations

ICE Table	$H_2CO_3(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$HCO_3^-(aq)$
Initial (M)	$0.033\ M$	-	0	0
Change (M)	$-x$	-	$+x$	$+x$
Equilibrium (M)	$0.033\ M - x$	-	x	x

Substituting the equilibrium concentrations into the equilibrium constant gives us:

$$K_{H_2CO_3} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Solving the preceding equation making our standard assumptions gives:

$$x = 1.2 \times 10^{-4}$$

Thus:

$$[H_2CO_3] = 0.033\ M$$

$$[H_3O^+] = [HCO_3^-] = 1.2 \times 10^{-4}\ M$$

2. Second Ionization: Determine the concentration of CO_3^{2-} in a solution at equilibrium.

Since the equilibrium step 1 is has a much bigger K_a than equilibrium step 2, we can the equilibrium conditions calculated from first part of example as the initial conditions for an ICER Table for the equilibrium step 2:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

ICER Table for the equilibrium step 2:

ICE Table	$HCO_3^-(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$CO_3^{2-}(aq)$
Initial (M)	$1.2 \times 10^{-4}\ M$	-	$1.2 \times 10^{-4}\ M$	0
Change (M)	$-y$	-	$+y$	$+y$
Equilibrium (M)	$1.2 \times 10^{-4}\ M - y$	-	$1.2 \times 10^{-4}\ M + y$	y

$$\begin{aligned} K_{HCO_3^-} &= \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} \\ &= \frac{(1.2 \times 10^{-4}\ M + y)(y)}{(1.2 \times 10^{-4}\ M - y)} \end{aligned}$$

To avoid solving a quadratic equation, we can assume $y \ll 1.2 \times 10^{-4}\ M$ so

$$K_{HCO_3^-} = 4.7 \times 10^{-11} \approx \frac{(1.2 \times 10^{-4}\ M)(y)}{(1.2 \times 10^{-4}\ M)}$$

Rearranging to solve for y

$$y \approx \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4}\ M)}{1.2 \times 10^{-4}\ M}$$

$$[\mathrm{CO_3^{2-}}] = y \approx 4.7 \times 10^{-11}$$

To summarize:

In part 1 of this example, we found that the $\mathrm{H_2CO_3}$ in a 0.033-M solution ionizes slightly and at equilibrium $[\mathrm{H_2CO_3}] = 0.033\ M$, $[\mathrm{H_3O^+}] = 1.2 \times 10^{-4}$, and $[\mathrm{HCO_3^-}] = 1.2 \times 10^{-4}\ M$. In part 2, we determined that $[\mathrm{CO_3^{2-}}] = 5.6 \times 10^{-11}\ M$.

Exercise 15.7.2: Hydrogen Sulfide

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 M. Calculate $[\mathrm{H_3O^+}]$, $[\mathrm{HS^-}]$, and $[\mathrm{S^{2\,-}}]$ in the solution:

$$\mathrm{H_2S}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HS^-}(aq) \qquad K_{\mathrm{a1}} = 8.9 \times 10^{-8}$$

$$\mathrm{HS^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{S^{2-}}(aq) \qquad K_{\mathrm{a2}} = 1.0 \times 10^{-19}$$

Answer

$[\mathrm{H_2S}] = 0.1M$, $[\mathrm{H_3O^+}] = [HS^-] = 0.0001\ M$, $[S^{2-}] = 1 \times 10^{-19}\ M$

We note that the concentration of the sulfide ion is the same as K_{a2}. This is due to the fact that each subsequent dissociation occurs to a lesser degree (as acid gets weaker).

Triprotic Acids

A triprotic acid is an acid that has three dissociable protons that undergo stepwise ionization: Phosphoric acid is a typical example:

- **The first ionization is**

$$\mathrm{H_3PO_4}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{H_2PO_4^-}(aq)$$

with $K_{\mathrm{a1}} = 7.5 \times 10^{-3}$.

- **The second ionization is**

$$\mathrm{H_2PO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HPO_4^{2-}}(aq)$$

with $K_{\mathrm{a2}} = 6.2 \times 10^{-8}$.

- **The third ionization is**

$$\mathrm{HPO_4^{2-}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{PO_4^{3-}}(aq)$$

with $K_{\mathrm{a3}} = 4.2 \times 10^{-13}$.

As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6. This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of $\mathrm{H_3PO_4}$ complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6, the calculations can be broken down into a series of parts similar to those for diprotic acids.

Polyprotic bases can accept more than one hydrogen ion in solution. The carbonate ion is an example of a diprotic base, since it can accept up to two protons. Solutions of alkali metal carbonates are quite alkaline, due to the reactions:

$$\mathrm{H_2O}(l) + \mathrm{CO_3^{2-}}(aq) \rightleftharpoons \mathrm{HCO_3^-}(aq) + \mathrm{OH^-}(aq)$$

and

$$\mathrm{H_2O}(l) + \mathrm{HCO_3^-}(aq) \rightleftharpoons \mathrm{H_2CO_3}(aq) + \mathrm{OH^-}(aq)$$

Summary

An acid that contains more than one ionizable proton is a polyprotic acid. The protons of these acids ionize in steps. The differences in the acid ionization constants for the successive ionizations of the protons in a polyprotic acid usually vary by roughly five orders of magnitude. As long as the difference between the successive values of K_a of the acid is greater than about a factor of 20, it is appropriate to break down the calculations of the concentrations of the ions in solution into a series of steps.

Glossary

diprotic acid

acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

diprotic base

base capable of accepting two protons. The protons are accepted in two steps

monoprotic acid

acid containing one ionizable hydrogen atom per molecule

stepwise ionization

process in which an acid is ionized by losing protons sequentially

triprotic acid

acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

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15.8: Organic Acids and Bases - Structure and Reactivity

Learning Objectives

- To understand how molecular structure affects the strength of an acid or base.

We have seen that the strengths of acids and bases vary over many orders of magnitude. In this section, we explore some of the structural and electronic factors that control the acidity or basicity of a molecule.

Bond Strengths

In general, the stronger the $\mathrm{A{-}H}$ or $\mathrm{B{-}H^+}$ bond, the less likely the bond is to break to form H^+ ions and thus the less acidic the substance. This effect can be illustrated using the hydrogen halides:

Relative Acid Strength	HF	HCl	HBr	HI
H–X Bond Energy (kJ/mol)	570	432	366	298
pKa	3.20	−6.1	−8.9	−9.3

The trend in bond energies is due to a steady decrease in overlap between the 1s orbital of hydrogen and the valence orbital of the halogen atom as the size of the halogen increases. The larger the atom to which H is bonded, the weaker the bond. Thus the bond between H and a large atom in a given family, such as I or Te, is weaker than the bond between H and a smaller atom in the same family, such as F or O. As a result, acid strengths of binary hydrides increase as we go down a column of the periodic table. For example, the order of acidity for the binary hydrides of Group 16 elements is as follows, with pK_a values in parentheses:

$$H_2O(14.00 = pK_w) < H_2S(7.05) < H_2Se(3.89) < H_2Te(2.6) \tag{15.8.1}$$

Stability of the Conjugate Base

Whether we write an acid–base reaction as $AH \rightleftharpoons A^- + H^+$ or as $BH^+ \rightleftharpoons B + H^+$, the conjugate base ($A^-$ or B) contains one more lone pair of electrons than the parent acid (AH or BH^+). Any factor that stabilizes the lone pair on the conjugate base favors dissociation of H^+ and makes the parent acid a stronger acid. Let’s see how this explains the relative acidity of the binary hydrides of the elements in the second row of the periodic table. The observed order of increasing acidity is the following, with pKa values in parentheses:

$$CH_4(\,50) \ll NH_3(\,36) < H_2O(14.00) < HF(3.20) \tag{15.8.2}$$

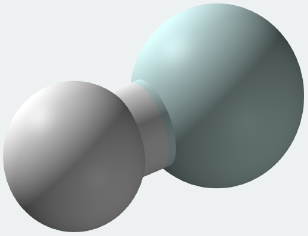
Consider, for example, the compounds at both ends of this series: methane and hydrogen fluoride. The conjugate base of CH_4 is CH_3^-, and the conjugate base of HF is F^-. Because fluorine is much more electronegative than carbon, fluorine can better stabilize the negative charge in the F^- ion than carbon can stabilize the negative charge in the CH3− ion. Consequently, HF has a greater tendency to dissociate to form H^+ and F^- than does methane to form H^+ and CH_3^-, making HF a much stronger acid than CH_4.

The same trend is predicted by analyzing the properties of the conjugate acids. For a series of compounds of the general formula HE, as the electronegativity of E increases, the E–H bond becomes more polar, favoring dissociation to form E^- and H^+. Due to both the increasing stability of the conjugate base and the increasing polarization of the E–H bond in the conjugate acid, acid strengths of binary hydrides increase as we go from left to right across a row of the periodic table.

> Acid strengths of binary hydrides increase as we go down a column or from left to right across a row of the periodic table.

the strongest acid Known: The hydrohelium Cation

The stornger acid, the weaker the covalent bond to a hydrogen atom. So the strongest acid possible is the molecule with the weakest bond. That is the hydrohelium (1+) cation, $\mathrm{HeH^+}$, which is a positively charged ion formed by the reaction of a proton with a helium atom in the gas phase. It was first produced in the laboratory in 1925 and is isoelectronic with molecular hydrogen (\ce{H2}). It is the strongest known acid, with a proton affinity of 177.8 kJ/mol.



Ball and stick model of the hydrohelium ion. (CC BY-SA 3.0; CCoil).

HeH^+ cannot be prepared in a condensed phase, as it would protonate any anion, molecule or atom with which it were associated. However it is possible to estimate a *hypothetical* aqueous acidity using Hess's law:

$HHe^+(g)$	→	$H^+(g)$	+ $He(g)$	+178 kJ/mol
$HHe^+(aq)$	→	$HHe^+(g)$		+973 kJ/mol
$H^+(g)$	→	$H^+(aq)$		−1530 kJ/mol
$He(g)$	→	$He(aq)$		+19 kJ/mol
$HHe^+(aq)$	→	$H^+(aq)$	+ $He(aq)$	−360 kJ/mol

A free energy change of dissociation of −360 kJ/mol is equivalent to a pK_a of −63.

It has been suggested that HeH^+ should occur naturally in the interstellar medium, but it has not yet been detected.

Inductive Effects

Atoms or groups of atoms in a molecule other than those to which H is bonded can induce a change in the distribution of electrons within the molecule. This is called an inductive effect, and, much like the coordination of water to a metal ion, it can have a major effect on the acidity or basicity of the molecule. For example, the hypohalous acids (general formula HOX, with X representing a halogen) all have a hydrogen atom bonded to an oxygen atom. In aqueous solution, they all produce the following equilibrium:

$$HOX_{(aq)} \rightleftharpoons H^+_{(aq)} + OX^-(aq) \tag{15.8.3}$$

The acidities of these acids vary by about three orders of magnitude, however, due to the difference in electronegativity of the halogen atoms:

HOX	Electronegativity of X	pKa
HOCl	3.0	7.40
HOBr	2.8	8.55
HOI	2.5	10.5

As the electronegativity of X increases, the distribution of electron density within the molecule changes: the electrons are drawn more strongly toward the halogen atom and, in turn, away from the H in the O–H bond, thus weakening the O–H bond and allowing dissociation of hydrogen as H^+.

The acidity of oxoacids, with the general formula $HOXO_n$ (with n = 0−3), depends strongly on the number of terminal oxygen atoms attached to the central atom X. As shown in Figure $15.8.1$, the K_a values of the oxoacids of chlorine increase by a factor of about 10^4 to 10^6 with each oxygen as successive oxygen atoms are added. The increase in acid strength with increasing number of terminal oxygen atoms is due to both an inductive effect and increased stabilization of the conjugate base.

> *Any inductive effect that withdraws electron density from an O–H bond increases the acidity of the compound.*

Because oxygen is the second most electronegative element, adding terminal oxygen atoms causes electrons to be drawn away from the O–H bond, making it weaker and thereby increasing the strength of the acid. The colors in Figure 15.8.1 show how the electrostatic potential, a measure of the strength of the interaction of a point charge at any place on the surface of the molecule, changes as the number of terminal oxygen atoms increases. In Figure 15.8.1 and Figure 15.8.2, blue corresponds to low electron densities, while red corresponds to high electron densities. The oxygen atom in the O–H unit becomes steadily less red from $HClO$ to $HClO_4$ (also written as $HOClO_3$, while the H atom becomes steadily bluer, indicating that the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. The decrease in electron density in the O–H bond weakens it, making it easier to lose hydrogen as H^+ ions, thereby increasing the strength of the acid.

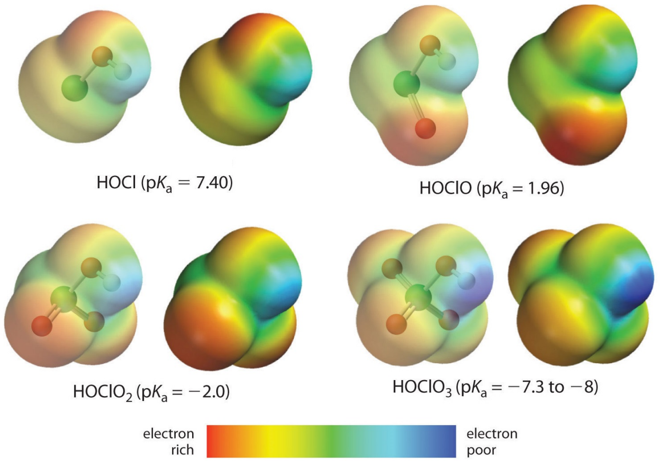
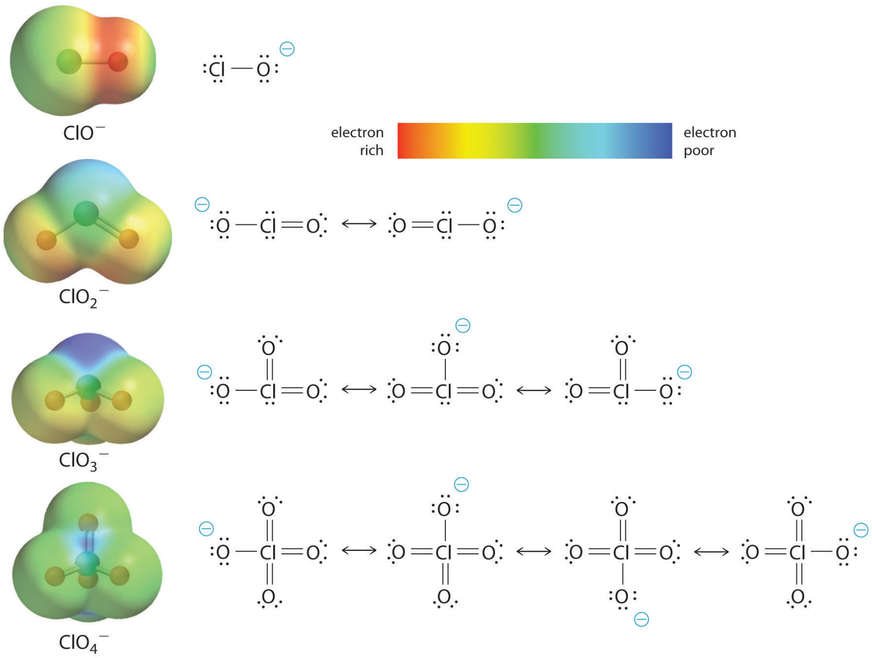


Figure 15.8.1: The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the O–H Unit. These electrostatic potential maps show how the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. Blue corresponds to low electron densities, whereas red corresponds to high electron densities. Source: Chlorine oxoacids pKa values from J. R. Bowser, Inorganic Chemistry (Pacific Grove, CA: Brooks-Cole,1993).

At least as important, however, is the effect of delocalization of the negative charge in the conjugate base. As shown in Figure 15.8.2, the number of resonance structures that can be written for the oxoanions of chlorine increases as the number of terminal oxygen atoms increases, allowing the single negative charge to be delocalized over successively more oxygen atoms.

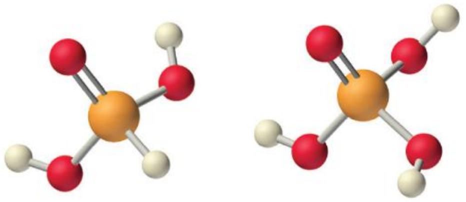
> *Electron delocalization in the conjugate base increases acid strength.*

The electrostatic potential plots in Figure 15.8.2 demonstrate that the electron density on the terminal oxygen atoms decreases steadily as their number increases. The oxygen atom in ClO− is red, indicating that it is electron rich, and the color of oxygen progressively changes to green in ClO_4^+, indicating that the oxygen atoms are becoming steadily less electron rich through the series. For example, in the perchlorate ion (ClO_4^-), the single negative charge is delocalized over all four oxygen atoms, whereas in the hypochlorite ion (OCl^-), the negative charge is largely localized on a single oxygen atom (Figure 15.8.2). As a result, the perchlorate ion has no localized negative charge to which a proton can bind. Consequently, the perchlorate anion has a much lower affinity for a proton than does the hypochlorite ion, and perchloric acid is one of the strongest acids known.



As the number of terminal oxygen atoms increases, the number of resonance structures that can be written for the oxoanions of chlorine also increases, and the single negative charge is delocalized over more oxygen atoms. As these electrostatic potential plots demonstrate, the electron density on the terminal oxygen atoms decreases steadily as their number increases. As the electron density on the oxygen atoms decreases, so does their affinity for a proton, making the anion less basic. As a result, the parent oxoacid is more acidic.

Similar inductive effects are also responsible for the trend in the acidities of oxoacids that have the same number of oxygen atoms as we go across a row of the periodic table from left to right. For example, H_3PO_4 is a weak acid, H_2SO_4 is a strong acid, and $HClO_4$ is one of the strongest acids known. The number of terminal oxygen atoms increases steadily across the row, consistent with the observed increase in acidity. In addition, the electronegativity of the central atom increases steadily from P to S to Cl, which causes electrons to be drawn from oxygen to the central atom, weakening the O–H bond and increasing the strength of the oxoacid.



phosphorous acid (H_3PO_3)

phosphoric acid (H_3PO_4)

Careful inspection of the data in Table $15.8.1$ shows two apparent anomalies: carbonic acid and phosphorous acid. If carbonic acid (H_2CO_3) were a discrete molecule with the structure $\text{(HO)}_2\text{C=O}$, it would have a single terminal oxygen atom and should be comparable in acid strength to phosphoric acid (H_3PO_4), for which pKa1 = 2.16. Instead, the tabulated value of pK_{a1} for carbonic acid is 6.35, making it about 10,000 times weaker than expected. As we shall see, however, H_2CO_3 is only a minor component of the aqueous solutions of CO_2 that are referred to as carbonic acid. Similarly, if phosphorous acid (H_3PO_3) actually had the structure $(HO)_3P$, it would have no terminal oxygen atoms attached to phosphorous. It would therefore be expected to be about as strong an acid as $HOCl$ (pKa = 7.40). In fact, the pK_{a1} for phosphorous acid is 1.30, and the structure of phosphorous acid is $\text{(HO)}_2\text{P(=O)H}$ with one H atom directly bonded to P and one P=O bond. Thus the pKa1 for phosphorous acid is similar to that of other oxoacids with one terminal oxygen atom, such as H_3PO_4. Fortunately, phosphorous acid is the only common oxoacid in which a hydrogen atom is bonded to the central atom rather than oxygen.

Table 15.8.1: Values of pKa for Selected Polyprotic Acids and Bases

Polyprotic Acids	Formula	pK_{a1}	pK_{a2}	pK_{a3}
carbonic acid*	“H_2CO_3”	6.35	10.33	
citric acid	$HO_2CCH-2C(OH)(CO_2H)CH_2CO_2H$	3.13	4.76	6.40
malonic acid	$HO-2CCH_2CO_2H$	2.85	5.70	
oxalic acid	HO_2CCO_2H	1.25	3.81	
phosphoric acid	H_3PO_4	2.16	7.21	12.32
phosphorous acid	H_3PO_3	1.3	6.70	
succinic acid	$HO_2CCH_2CH_2CO_2H$	4.21	5.64	
sulfuric acid	H_2SO_4	−2.0	1.99	
sulfurous acid*	“H_2SO_3”	1.85	7.21	
Polyprotic Bases	**Formula**	pK_{b1}	pK_{b2}	
ethylenediamine	$H_2N(CH_2)_2NH_2$	4.08	7.14	
piperazine	$HN(CH_2CH_2)_2NH$	4.27	8.67	
propylenediamine	$H_2N(CH_2)_3NH_2$	3.45	5.12	

*H_2CO_3 and H_2SO_3 are at best minor components of aqueous solutions of $CO_{2(g)}$ and $SO_{2(g)}$, respectively, but such solutions are commonly referred to as containing carbonic acid and sulfurous acid, respectively.

Inductive effects are also observed in organic molecules that contain electronegative substituents. The magnitude of the electron-withdrawing effect depends on both the nature and the number of halogen substituents, as shown by the pKa values for several acetic acid derivatives:

$$pK_aCH_3CO_2H4.76<CH_2ClCO_2H2.87<CHCl_2CO_2H1.35<CCl_3CO_2H0.66<CF_3CO_2H0.52$$

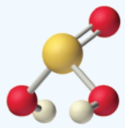
As you might expect, fluorine, which is more electronegative than chlorine, causes a larger effect than chlorine, and the effect of three halogens is greater than the effect of two or one. Notice from these data that inductive effects can be quite large. For instance, replacing the $-\mathrm{CH_3}$ group of acetic acid by a $-\mathrm{CF_3}$ group results in about a 10,000-fold increase in acidity!

✓ Example 15.8.1

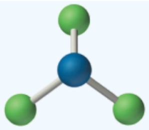
Arrange the compounds of each series in order of increasing acid or base strength.

a. sulfuric acid [H_2SO_4, or $(HO)_2SO_2$], fluorosulfonic acid (FSO_3H, or FSO_2OH), and sulfurous acid [H_2SO_3, or $(HO)_2SO$]
b. ammonia (NH_3), trifluoramine (NF_3), and hydroxylamine (NH_2OH)

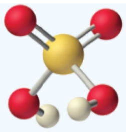
The structures are shown here.



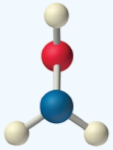
sulfurous acid
(H_2SO_3)



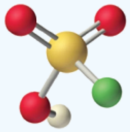
trifluoramine
(NF_3)



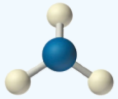
sulfuric acid
(H_2SO_4)



hydroxylamine
(NH_2OH)



fluorosulfonic acid
(FSO_3H)



ammonia
(NH_3)

Given: series of compounds

Asked for: relative acid or base strengths

Strategy:

Use relative bond strengths, the stability of the conjugate base, and inductive effects to arrange the compounds in order of increasing tendency to ionize in aqueous solution.

Solution:

Although both sulfuric acid and sulfurous acid have two –OH groups, the sulfur atom in sulfuric acid is bonded to two terminal oxygen atoms versus one in sulfurous acid. Because oxygen is highly electronegative, sulfuric acid is the stronger acid because the negative charge on the anion is stabilized by the additional oxygen atom. In comparing sulfuric acid and fluorosulfonic acid, we note that fluorine is more electronegative than oxygen. Thus replacing an –OH by –F will remove more electron density from the central S atom, which will, in turn, remove electron density from the S–OH bond and the O–H bond. Because its O–H bond is weaker, FSO_3H is a stronger acid than sulfuric acid. The predicted order of acid strengths given here is confirmed by the measured pKa values for these acids:

$$pKaH_2SO_3 1.85 < H_2SO_4^{-2} < FSO_3H - 10$$

The structures of both trifluoramine and hydroxylamine are similar to that of ammonia. In trifluoramine, all of the hydrogen atoms in NH3 are replaced by fluorine atoms, whereas in hydroxylamine, one hydrogen atom is replaced by OH. Replacing the three hydrogen atoms by fluorine will withdraw electron density from N, making the lone electron pair on N less available to bond to an H^+ ion. Thus NF_3 is predicted to be a much weaker base than NH_3. Similarly, because oxygen is more electronegative than hydrogen, replacing one hydrogen atom in NH_3 by OH will make the amine less basic. Because oxygen is less electronegative than fluorine and only one hydrogen atom is replaced, however, the effect will be smaller. The predicted order of increasing base strength shown here is confirmed by the measured pK_b values:

$$pK_b NF_3 — << NH_2OH 8.06 < NH_3 4.75$$

Trifluoramine is such a weak base that it does not react with aqueous solutions of strong acids. Hence its base ionization constant has never been measured.

? Exercise 15.8.1

Arrange the compounds of each series in order of

a. decreasing acid strength: H_3PO_4, $CH_3PO_3H_2$, and $HClO_3$.
b. increasing base strength: CH_3S^-, OH^-, and CF_3S^-.

Answer a

$HClO-3 > CH_3PO_3H_2 > H_3PO_4$

Answer a

$CF_3S^- < CH_3S^- < OH^-$

Summary

Inductive effects and charge delocalization significantly influence the acidity or basicity of a compound. The acid–base strength of a molecule depends strongly on its structure. The weaker the A–H or B–H+ bond, the more likely it is to dissociate to form an H^+ ion. In addition, any factor that stabilizes the lone pair on the conjugate base favors the dissociation of H^+, making the conjugate acid a stronger acid. Atoms or groups of atoms elsewhere in a molecule can also be important in determining acid or base strength through an inductive effect, which can weaken an $\mathrm{O–H}$ bond and allow hydrogen to be more easily lost as H^+ ions.

Contributors and Attributions

-
    - Anonymous

15.9: A Deeper Look - Exact Treatment of Acid-Base Equilibria

Learning Objectives

- Calculate the pH when two weak acids are present in a solution.
- Calculate the pH when the concentration of the acid is very dilute.
- Calculate the pH by including the autoionization of water.

A common paradigm in solving for pHs in weak acids and bases is that the equilibria of solutions containing one weak acid or one weak base. In most cases, the amount of $\mathrm{H^+}$ from the autoionization of water is negligible. For very dilute solutions, the amount of $\mathrm{H^+}$ ions from the autoionization of water must also be taken into account. Thus, a strategy is given here to deal with these systems.

When two or more acids are present in a solution, the concentration of $\mathrm{H^+}$ (or pH) of the solution depends on the concentrations of the acids and their acidic constants K_a. The hydrogen ion is produced by the ionization of all acids, but the ionizations of the acids are governed by their equilibrium constants, K_a's. Similarly, the concentration of $\mathrm{OH^-}$ ions in a solution containing two or more weak bases depends on the concentrations and K_b values of the bases. For simplicity, we consider two acids in this module, but the strategies used to discuss equilibria of two acids apply equally well to that of two bases.

Dissociation of Acids and Bases in Water Couple Two Equilibria with a Common Ion H$^+$

If the pH is between 6 and 8, the contribution due to autoionization of water to $[\mathrm{H^+}]$ should also be considered. When autoionization of water is considered, the method is called the **exact pH calculation** or the **exact treatment**. This method is illustrated below. When the contribution of pH due to self-ionization of water cannot be neglected, there are two coupled equilibria to consider:

$$\mathrm{HA \rightleftharpoons H^+ + A^-} \tag{15.9.1}$$

ICE Table	HA	$\mathrm{H^+}$	$\mathrm{A^-}$
Initial	C	0	0
Change	$-x$	x	x
Equilibrium	$C-x$	x	x

and

$$\mathrm{H_2O \rightleftharpoons H^+ + OH^-} \tag{15.9.2}$$

ICE Table	$\mathrm{H_2O}$	$\mathrm{H^+}$	$\mathrm{OH^-}$
Equilibrium	-	y	y

Thus,

$$[\mathrm{H^+}] = (x+y) \tag{15.9.3}$$

$$[\mathrm{A^-}] = x \tag{15.9.4}$$

$$[\mathrm{OH^-}] = y \tag{15.9.5}$$

and the two equilibrium constants are

$$K_\mathrm{a} = \frac{(x+y)\,x}{C-x} \tag{15.9.6}$$

and

$$K_\mathrm{w} = (x+y)\,y \tag{15.9.7}$$

Although you may use the method of successive approximation, the formula to calculate the pH can be derived directly from Equations 15.9.6 and 15.9.7. Solving for x from Equation 15.9.7 gives

$$x=\frac{K_{\mathrm{w}}}{y}-y \tag{15.9.8}$$

and substituting this expression into 15.9.6 results in

$$K_{\mathrm{a}}=\frac{(x+y)\left(\frac{K_{\mathrm{w}}}{y}-y\right)}{C-\frac{K_{\mathrm{w}}}{y}+y} \tag{15.9.9}$$

Rearrange this equation to give:

$$\begin{aligned}\left[\mathrm{H}^{+}\right] &=(x+y) && (15.9.10)\\ &=\frac{C-\frac{K_{\mathrm{w}}}{y}+y}{\frac{K_{\mathrm{w}}}{y}-y}K_{\mathrm{a}} && (15.9.11)\end{aligned}$$

Note that

$$\frac{K_{\mathrm{w}}}{y}=\left[\mathrm{H}^{+}\right] \tag{15.9.12}$$

so

$$y=\frac{K_{\mathrm{w}}}{\left[\mathrm{H}^{+}\right]}. \tag{15.9.13}$$

Thus, we get:

$$\left[\mathrm{H}^{+}\right]=\frac{C-\left[\mathrm{H}^{+}\right]+\frac{K_{\mathrm{w}}}{\left[\mathrm{H}^{+}\right]}}{\left[\mathrm{H}^{+}\right]-\frac{K_{\mathrm{w}}}{\left[\mathrm{H}^{+}\right]}}K_{\mathrm{a}} \tag{15.9.14}$$

As written, Equation 15.9.14 is complicated, but can be put into a polynomial form

$$\left[\mathrm{H}^{+}\right]^{3}+K_{\mathrm{a}}\left[\mathrm{H}^{+}\right]^{2}-\left(K_{\mathrm{w}}+CK_{\mathrm{a}}\right)\left[\mathrm{H}^{+}\right]-K_{\mathrm{w}}K_{\mathrm{a}}=0 \tag{15.9.15}$$

Solving for the exact hydronium concentration requires solving a third-order polynomial. While this is analytically feasible, it is an awkward equation to handle. Instead, we often consider two approximations to Equation 15.9.15 that can made under limiting conditions.

Case 1: High Concentration Approximation

If $[H^{+}]>1\times 10^{-6}$, then

$$\frac{K_{w}}{[H^{+}]}<1\times 10^{-8}. \tag{15.9.16}$$

This is small indeed compared to $[H^{+}]$ and C in Equation 15.9.14. Thus,

$$[H^{+}]\approx\frac{C-[H^{+}]}{[H^{+}]}K_{\mathrm{a}} \tag{15.9.17}$$

$$[H^{+}]^{2}+K_{\mathrm{a}}[H^{+}]-CK_{\mathrm{a}}\approx 0 \tag{15.9.18}$$

Equation 15.9.18 is a quadratic equation with two solutions. However, only one will be positive and real:

$$[H^{+}]\approx\frac{-K_{\mathrm{a}}+\sqrt{K_{\mathrm{a}}^{2}+4CK_{\mathrm{a}}}}{2} \tag{15.9.19}$$

Case 2: Low Concentration Approximation

If $[H^+] \ll C$, then

$$C - [H^+] \approx C \tag{15.9.20}$$

Equation 15.9.14can be simplified

$$[H^+] \approx \frac{C}{[H^+]} K_\mathrm{a} \tag{15.9.21}$$

$$[H^+] \approx \sqrt{CK_\mathrm{a}} \tag{15.9.22}$$

The treatment presented in deriving Equation 15.9.14is more general, and may be applied to problems involving two or more weak acids in one solution.

Example 15.9.1

Calculate the $[\mathrm{H^+}]$, $[\mathrm{Ac^-}]$, and $[\mathrm{Cc^-}]$ when the solution contains 0.200 M HAc ($K_a = 1.8 \times 10^{-5}$), and 0.100 M HCc (the acidity constant $K_c = 1.4 \times 10^{-3}$). (HAc is acetic acid whereas HCc is chloroacetic acid).

Solution

Assume x and y to be the concentrations of $\mathrm{Ac^-}$ and $\mathrm{Cc^-}$, respectively, and write the concentrations below the equations:

$$\begin{array}{ccccc} \mathrm{HAc} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{Ac^-} \\ 0.200 - x & & x & & x \end{array}$$

$$\begin{array}{ccccc} \mathrm{HCc} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{Cc^-} \\ 0.100 - y & & y & & y \end{array}$$

$$[\mathrm{H^+}] = (x + y)$$

Thus, you have

$$\frac{(x+y)\,x}{0.200 - x} = 1.8 \times 10^{-5} \tag{15.9.23}$$

$$\frac{(x+y)\,y}{0.100 - y} = 1.4 \times 10^{-3} \tag{15.9.24}$$

Solving for x and y from Equations 15.9.23and 15.9.24may seem difficult, but you can often make some assumptions to simplify the solution procedure. Since HAc is a weaker acid than is HCc, you expect x << y. Further, y << 0.100. Therefore, $x + y \approx y$ and 0.100 - y => 0.100. Equation 15.9.24becomes:

$$\frac{(y)\,y}{0.100} = 1.4 \times 10^{-3} \tag{15.9.25}$$

which leads to

$$\begin{aligned} y &= (1.4 \times 10^{-3} \times 0.100)^{1/2} \\ &= 0.012 \end{aligned}$$

Substituting y in Equation 15.9.23results in

$$\frac{(x + 0.012)\,x}{0.200 - x} = 1.8 \times 10^{-5} \tag{15.9.26}$$

This equation is easily solved, but you may further assume that $0.200 - x \approx 0.200$, since $x << 0.200$. Thus,

$$\begin{aligned} x &= \frac{-0.012 + (1.44 \times 10^{-4} + 1.44 \times 10^{-5})^{1/2}}{2} \\ &= 2.9 \times 10^{-4} \quad \longleftarrow \text{Small indeed compared to 0.200} \end{aligned}$$

You had a value of 0.012 for y by neglecting the value of x in Equation 15.9.24. You can now recalculate the value for y by substituting values for x and y in Equation 15.9.24.

$$\frac{(2.9 \times 10^{-4} + y)\, y}{0.100 - 0.012} = 1.4 \times 10^{-3} \tag{15.9.27}$$

Solving for y in the above equation gives

$$y = 0.011$$

You have improved the y value from 0.012 to 0.011. Substituting the new value for y in a successive approximation to recalculate the value for x improves its value from 2.9×10^{-4} to a new value of 3.2×10^{-4}. Use your calculator to obtain these values. Further refinement does not lead to any significant changes for x or y.

Discussion

You should write down these calculations on your note pad, since reading alone does not lead to thorough understanding.

Example 15.9.2

A weak acid HA has a K_a value of 4.0×10^{-11}. What are the pH and the equilibrium concentration of A^- in a solution of 0.0010 M HA?

Solution

For the solution of this problem, two methods are given here. If you like the x and y representation, you may use method (a).

Method (a)

The two equilibrium equations are:

$$\begin{array}{ccccc} \mathrm{HA} & \rightleftharpoons & \mathrm{H}^+ & + & \mathrm{A}^-; \\ 0.0010 - x & & x & & x \\ \\ \mathrm{H_2O} & \rightleftharpoons & \mathrm{H}^+ & + & \mathrm{OH}^- \\ & & y & & y \end{array} \tag{15.9.28}$$

$$[\mathrm{H}^+] = (x + y) \tag{15.9.29}$$

$$\frac{(x + y)\, x}{0.0010 - x} = 4.0 \times 10^{-}11 \tag{15.9.30}$$

$$\tag{15.9.31}$$

$$(x + y)\, y = 1 \times 10^{-}14 \tag{15.9.32}$$

Assume y << x, and x << 0.0010, then you have

$$\frac{(x)\, x}{0.0010} = 4.0 \times 10^{-11} \tag{15.9.33}$$

$$x = (0.0010 \times 4.0e^{-11})^{1/2} \tag{15.9.34}$$

$$= 2.0 \times 10^{-7} \tag{15.9.35}$$

Substituting $2.0 \times^{-7}$ for x in 4 and solving the quadratic equation for y gives,

$$(2.0 \times 10^{-}7 + y)\, y = 1 \times 10^{-14}$$

$$y = 4.1 \times 10^{-8}$$

Substituting 4.1×10^{-8} in Equation 15.9.30, but still approximating 0.0010-x by 0.0010:

$$\frac{(x + 4.1 \times 10^{-8})\, x}{0.0010} = 4.0 \times 10^{-11} \tag{15.9.36}$$

Solving this quadratic equation for a positive root results in

$$x = 1.8 \times 10^{-7}\ \mathrm{M} \longleftarrow \text{Recall } x = [\mathrm{A}^-]$$

$$\begin{aligned}[\mathrm{H}^+] &= x + y \\ &= (1.8 + 0.41)\, 1 \times 10^{-7} \\ &= 2.2 \times 10^{-7} \\ \mathrm{pH} &= 6.65\end{aligned}$$

The next method uses the formula derived earlier.

Method (b)

Using the formula from the exact treatment, and using 2×10^{-7} for all the $[\mathrm{H}^+]$ values on the right hand side, you obtain a new value of $[\mathrm{H}^+]$ on the left hand side,

$$\begin{aligned}[\mathrm{H}^+] &= \frac{C - [\mathrm{H}^+] + \dfrac{K_\mathrm{w}}{[\mathrm{H}^+]}}{[\mathrm{H}^+] - \dfrac{K_\mathrm{w}}{[\mathrm{H}^+]}} K_\mathrm{a} \\ &= 2.24 \times 10^{-7} \\ \mathrm{pH} &= 6.65\end{aligned}$$

The new $[\mathrm{H}^+]$ enables you to recalculate $[\mathrm{A}^-]$ from the formula:

$$\begin{aligned}(2.24 \times 10^{-7})[\mathrm{A}^-] &= C K_\mathrm{a} \\ [\mathrm{A}^-] &= \frac{(0.0010)(4.0 \times 10^{-11})}{2.24 \times 10^{-7}} \\ &= 1.8 \times 10^{-7}\end{aligned}$$

DISCUSSION

You may have attempted to use the approximation method:

$$\begin{aligned}x &= (C K_\mathrm{a})^{1/2} \\ &= 2.0 \times 10^{-7}\ \mathrm{M\ A^-},\ \text{or } \mathrm{H}^+;\ \mathrm{pH} = 6.70\end{aligned}$$

and obtained a pH of 6.70, which is greater than 6.65 by less than 1%. However, when an approximation is made, you have no confidence in the calculated pH of 6.70.

Summary

Water is both an acid and a base due to the autoionization,

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H}^+ + \mathrm{OH}^-$$

However, the amount of H^+ ions from water may be very small compared to the amount from an acid if the concentration of the acid is high. When calculating $[\mathrm{H}^+]$ in an acidic solution, approximation method or using the quadratic formula has been discussed in the modules on weak acids.

Contributors and Attributions

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15.E: Acid-Base Equilibria (Exercises)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

Q3

Vinegar contains acetic acid CH_3COOH. What species serves as a base when vinegar is mixed with baking soda, sodium bicarbonate, during the preparation of bread?

Solution

$$NaHCO_3 + CH_3COOH \rightarrow NaCH_3COO + CO_2 + H_2O$$

$NaHCO_3$ serves as the base.

Q7

a. Thinking of acid-base reaction in terms of oxide donors and oxide acceptors, is the base oxide donors or oxide acceptors?
b. Identify the acid and base in the reaction:

$$\mathrm{CaO + CO_2 \rightleftharpoons CaCO_3}$$

Solution

a. The base is the oxide donor. We can distinctly see this in the autoionization of H_2O, where OH^- counts as the basic part
b. CaO is the base, and CO_2 is the acid.

Q5

Baking soda known as $\mathrm{NaHCO_3}$ is formed by adding water and carbon dioxide to sodium carbonate.

a. Write a balanced equation for this chemical reaction
b. Is this a Brønsted-Lowry acid-base reaction? What is a Brønsted-Lowry acid? What is a Brønsted-Lowry base?

Solution

a. $\mathrm{Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3}$
b. This is not a Brønsted-Lowry acid-base reaction because it does not involve a transfer of an H^+ ion. A Brønsted-Lowry acid is a proton donor, and a Brønsted-Lowry base is a proton acceptor.

Q9

Identify each of the following oxides as an acid or base anhydride:

a. CaO
b. $\mathrm{P_2O_5}$

Solution

a. CaO is the base anhydride of calcium hydroxide $\mathrm{Ca(OH)_2}$.
b. $\mathrm{P_2O_5}$ is the acid anhydride of phosphoric acid $\mathrm{H_3PO_4}$.

Q11

Al(III) oxide is amphorteric. What is the balanced chemical equation of Al(III) oxide react with aqueous $\mathrm{H_2SO_4}$? What is the balanced equation of it reacts with KOH?

Solution

$$\mathrm{Al_2O_3(s) + 3\,H_2SO_4(aq) \rightleftharpoons Al_2(SO_4)_3(aq) + 3\,H_2O(l)}$$

$$\boxed{\text{\ce\{Al2O3 + 2KOH + 3H2O \rightleftharpoons 2KAl(OH)4 \nonumber}}$$

Q13

The $[\mathrm{H_3O^+}]$ concentration in a glass of orange juice is 3.96 x 10^{-5} M. What is the juice's pH?

Solution

$$pH = -\log[H_3O+]$$

Since the concentration of hydronium ions is given, the pH calculation is as follows:

$$pH = -\log[3.96 \times 10^{-5}] = 4.4023$$

pH is a measure of hydrogen ions in a solution. This concentration defines the acidity or alkalinity of a solution.

Q17

The $\mathrm{pK_w}$ of an unknown salty water at 25 °C is 13.665. This differs from the usual $\mathrm{K_w}$ of 14.00 at this temperature because dissolved salts make this unknown salty water a non- ideal solution. If the pH in the salty water is 7.8, what are the concentrations of H_3O^+ and OH^- in the salty water at 25 °C?

Solution

$\mathrm{pH} = -\log[\mathrm{H_3O^+}]$, hence,

$[\mathrm{H_3O^+}] = 10^{-7.8} = 1.5849 \times 10^{-}8\ \mathrm{M}$

Since $\mathrm{pK_w} = [\mathrm{OH^-}][\mathrm{H_3O^+}]$,

$[\mathrm{OH^-}] = \frac{10^{-13.665}}{1.5849 \times 10^{-8}\ \mathrm{M}} = 1.3645 \times 10^{-6}\mathrm{M}$

Q19

When rubidium (Rb) solid is added to water, there is an instantaneous and vigorous reaction (i.e., an explosion) as this video demonstrates. Based on this information, which of these two equations is a more accurate representation the reaction?

$$2\,\mathrm{Rb(s)} + 2\,\mathrm{H_2O(l)} \rightarrow 2\,\mathrm{RbOH(aq)} + \mathrm{H_2(aq)}$$

$$2\,\mathrm{Rb(s)} + 2\,\mathrm{H_3O^+(aq)} \rightarrow 2\,\mathrm{Rb^+(aq)} + \mathrm{H_2(aq)} + 2\,\mathrm{H_2O(l)}$$

Solution

The equation:

$$2\,\mathrm{Rb(s)} + 2\,\mathrm{H_2O(l)} \rightarrow 2\,\mathrm{RbOH(aq)} + \mathrm{H_2(aq)}$$

Is a better representation of Rb being placed into water. It represents the direct interaction between the alkali metal and water. We know from the problem that the reaction is fast, vigorous, and forceful. The second equation represents a reaction in equilibrium, one that we would expect to be slow as there are only 1x10^{-7}mol/L of H_3O^+ in a 1L of water. Even if the reaction were vigorous at the low concentration of hydronium ions, there would not be enough of them to keep up with the speed of the reaction (they would become a limiting reactant), hence slowing or stopping the reaction from proceeding.

Q23

In the following chemical equation determine which species is the strongest acid and which is the strongest base, using the Brønsted–Lowry definition. At equilibrium, is there a greater concentration of reactants or products present?

a. $$\mathrm{HIO_3}_{\ (aq)} + \mathrm{HCOO^-_{(aq)}} \rightleftharpoons \mathrm{HCOOH_{(aq)}} + \mathrm{IO_3^-}_{\ (aq)}$$

b. $$\left(\mathrm{HIO_3}_{\ (aq)} \rightleftharpoons \mathrm{IO_3^-}_{\ (aq)} \qquad \mathrm{K_a} = 1 \cdot 6 \times 10^{-1}\right)$$

c. $$\left(\mathrm{HCOOH_{(aq)}} \rightleftharpoons \mathrm{HCOO^-_{(aq)}} \qquad \mathrm{K_a} = 1 \cdot 8 \times 10^{-4}\right)$$

Solution

A Brønsted–Lowry acid is the species that donates protons in a solution. When comparing two different weak acids in solution, like:

$$HIO_{3\ (aq)} + HCOO^-_{(aq)} \rightleftharpoons HCOOH_{(aq)} + IO^-_{3\ (aq)}$$

We can compare their abilities to donate protons to see which one is the stronger of the two weak acids.

$$HIO_{3\ (aq)} + H_2O_{(aq)} \rightleftharpoons IO^-_{3\ (aq)} + H_3O^+_{(aq)} \qquad K_a = 1 \cdot 6 \times 10^{-1}$$

$$HCOOH_{(aq)} + H_2O_{(aq)} \rightleftharpoons HCOO^-_{(aq)} + H_3O^+_{(aq)} \qquad K_a = 1 \cdot 8 \times 10^{-4}$$

Seeing that $K_a = 1 \cdot 6 \times 10^{-1} > K_a = 1 \cdot 8 \times 10^{-4}$, we know HIO_3 is the stronger acid.

A Brønsted–Lowry base is the species that accepts protons. So in this case, we must examine which of the two weak acids has a stronger conjugate base, which means we must find the K_b for the reactions of the conjugate bases.

We know that:

$$K_w = K_a \times K_b$$

and

$$K_w = 1.0 \times 10^{-7}$$

So we can find K_b by dividing K_w by K_a which ultimately gives us:

$$IO^-_{3\ (aq)} + H_2O_{(aq)} \rightleftharpoons HIO_{3\ (aq)} + OH^-_{(aq)} \qquad K_b = 6 \cdot 3 \times 10^{-14}$$

$$HCOO^-_{(aq)} + H_2O_{(aq)} \rightleftharpoons HCOOH_{(aq)} + OH^-_{(aq)} \qquad K_b = 5 \cdot 6 \times 10^{-11}$$

Seeing that $K_b = 5 \cdot 6 \times 10^{-11} > K_a = 6 \cdot 3 \times 10^{-14}$, we know $HCOO^-$ is the stronger base.

To determine whether there is a greater concentration of reactants or products present, the K value for the overall reaction must be determined. The overall reaction is the product of the first given reaction and the reverse of the second given reaction. Dividing the first value for K_a by the second gives

$$K = 888$$

$$K > 1$$

which indicates that at equilibrium, there is a greater concentration of products than reactants.

Q27

Acetic acid gives vinegar a sour taste and strong aroma. Its K_a value is 1.75 x 10^{-5}. What is the pH of the solution if 0.59 grams of acetic acid is dissolved in 40 mL of water?

Solution

First, convert grams of acetic acid to moles.

$$(0.59\ g\ CH_3COOH)\left(\frac{1\ mol}{60.05\ g\ CH_3COOH}\right) = 0.0098\ mol$$

Then, find the molarity of acetic acid by dividing the number of moles of acetic acid by the number of liters of water.

$$\frac{0.0098\ mol}{0.04\ L\ water} = 0.246\ M$$

Using the molarity and K_a, construct and solve an ICE table to find out how much the acetic acid dissociates.

$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$

	CH_3COOH	H_2O	CH_3COO^-	H_3O^+

I	0.246	---	0	0
C	-x	---	+x	+x
E	0.246-x	---	x	x

The acid dissociation constant works in the below equation:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Plug in the final concentration values from the ICE table and solve for x.

$$1.75 \times 10^{-5} = \frac{x^2}{0.246 - x}$$

$$x = 0.0021$$

Use the calculated value of x to calculate the concentration of H_3O+, which in this case is equal to x. Then, plug this concentration into the equation for pH.

$$pH = -log[0.0021]$$

$$pH = 2.6848$$

Q29

a. A student prepares a solution of 0.60M of formic acid carefully in a water bath that remains constant at 25°C, determine the pH of the solution. (Ka of formic acid: 1.8×10^{-4})
b. How many grams of trichloroacetic acid should be dissolved per liter of deionized water so that the solution of trichloroacetic acid would have the same pH as that of the formic acid solution in a)? (Ka of trichloroacetic acid is 2.2×10^{-1})

Solution

Construct an ICE table based on the equation:

$$\mathrm{HCOOH + H_2O \rightleftharpoons HCO_2^- + H_3O^+}$$

	$HCOOH$	H_2O	HCO_2^-	H_3O^+
I	0.6	-	0	0
C	-x	-	+x	+x
E	0.6-x	-	x	x

Ka can then be equated to an algebraic expression:

$$\mathrm{Ka} = \frac{\mathrm{x}^2}{0.6 - \mathrm{x}}$$

$$1.8 \times 10^{-4} = \frac{\mathrm{x}^2}{0.6 - \mathrm{x}}$$

$$\mathrm{x} = 0.0103026$$

or

$$\mathrm{x} = -0.0104$$

x must be postive. Thus, x = 0.0103026.

$$[\mathrm{H_3O^+}]$$

$$\mathrm{pH} = -\log(0.0103026) = 1.987$$

Because we know the pH we want to attain (1.987), we have start by first finding $[\mathrm{H_3O^+}]$:

$$-\log[\mathrm{H_3O^+}] = 1.987$$

$$[\mathrm{H_3O^+}] = 10^{-1.987}$$

$$[\mathrm{H_3O^+}] = 0.0103026$$

An ICE table can also be constructed for the reaction:

$$CCl_3CO_2H + H_2O \rightleftharpoons CCl_3CO_2^- + H_3O^+$$

	CCl_3CO_2H	H_2O	$CCl_3CO_2^-$	H_3O^+
I	x	-	0	0
C	-0.010303	-	+0.010303	+0.010303
E	x-0.010303	-	0.010303	0.010303

$$\mathrm{K_a} = \frac{(0.010303)^2}{(\mathrm{x} - 0.010303)}$$

$$2.2 \times 10^{-1} = \frac{(0.010303)^2}{(\mathrm{x} - 0.010303)}$$

$$\mathrm{x} = 0.0107855\mathrm{M}$$

To calculate the mass of trichloroacetic acid, we can calculate the molarity of trichloroacetic acid by its molar mass.

$$\text{Mass of trichloroacetic acid} = 0.0107855\ \mathrm{M} \times (35.5\frac{\mathrm{g}}{\mathrm{mol}} \times 3 + 12\frac{\mathrm{g}}{\mathrm{mol}} \times 2 + 16\frac{\mathrm{g}}{\mathrm{mol}} \times 2 + 1\frac{\mathrm{g}}{\mathrm{mol}}) = 1.76\ \mathrm{g}$$

Q41

Rank each of the 0.2 M solution below in an order of increasing pH: NH_4I, KF, HCl, KCl, KOH.

Solution

$$HCl < NH_4I < KF < KCl < KOH$$

Q43

0.040 mol of Diethylamine ($\mathrm{C_4H_{11}N}$, $\mathrm{pK_b}$ =11.09) is titrated with 0.015 mol of HCl in a 1.00L wash bottle, calculate the pH value of the solution.

Solution

Because equivalence point is not reached yet, we can employ Henderson-Hasselbalch equation.

$$pOH \approx pK_b + \log \frac{[BH^+]}{[B]}$$

$$pOH \approx (11.09) + \log \frac{[C_4H_{12}N^+]}{[C_4H_{11}N]}$$

$$pOH \approx (11.09) + \log \frac{0.015}{0.040-15}$$

$$pOH \approx 10.87$$

At room temperature $K_w = 14$ and

$$\begin{aligned} pH &= pK_w - pOH \\ &= 14.00 - 10.87 \\ &= 3.13 \end{aligned}$$

Q45

Prepare a Hypochlorous acid/Hypochlorite buffer at pH 7.

a. Suppose you only have 0.5 mol of lithium hypochlorite, but an infinite supply of hypochlorous acid (pKa = 7.53) and water. How many moles of hypochlorous acid should you use, assuming you use all 0.5 mol of lithium hypochlorite, and dilute the buffer to 100 mL?
b. Suppose Professor Güntherfœrd's arm was doused in about 0.12 moles total HCl. Will this buffer be enough to bring her arm up to a pH over 6.5?

Solution

Using the Henderson–Hasselbalch approximation:

$$\mathrm{pH} \approx \mathrm{pK_a} + \log \frac{[\mathrm{ClO^-}]_o}{[\mathrm{HClO}]_o}$$

It's easy to re-arrange the equation to solve for $[\mathrm{HClO}]_\circ$. Multiplying by 100 mL yields the moles of acid added.

$$\mathrm{pH} \approx \mathrm{pK_a} + \log \frac{[\mathrm{ClO^-}]_o}{[\mathrm{HClO}]_o}$$

$$7 \approx \mathrm{pK_a} + \log \frac{[\mathrm{ClO^-}]_o}{[\mathrm{HClO}]_o}$$

$$7 \approx 7.53 + \log \frac{5}{[\mathrm{HClO}]_o}$$

$$[\mathrm{HClO}]_\circ \approx 16.94$$

$$\text{Moles HClO} \approx 1.694$$

Q49

A student is given 500 mL of a 0.500 M acetic acid solution and wants to create a pH 5.0 buffer. How many mL of 1 M NaOH must be added to the original solution? Acetic acid has a $\mathrm{pK_a}$ of 4.756.

Solution

We first use the Henderson-Hasselbach approximation to determine the required ratio of base to acid in the solution:

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$

$$5.00 = 4.756 + \log\left(\frac{[base]}{[acid]}\right)$$

$$0.244 = \log\left(\frac{[base]}{[acid]}\right)$$

$$1.75 = \frac{[base]}{[acid]}$$

Next, we will determine the molar amount of base required to get a pH of 5.00. In order to simplify things we will first solve for the molar quantities as of each using the simple ratio above in relation to 1.75:

$$\begin{aligned}\text{Acetic Acid in 500 mL solution} &= (0.5\ M) \times (0.5\ L) \\ &= 0.25\ mol\end{aligned}$$

$$NaOH\ in\ 500\ mL\ solution = (0.25\ mol) \times (1.75) + 0.25 = 0.6875 +\ mol$$

Now we'll determine the volume of 1M NaOH needed to raise the pH:

$$\left(\frac{1\ mol}{1\ L}\right) = \left(\frac{0.6875\ mol}{x}\right)$$

$$s = 0.6875\ L\ NaOH$$

Now we'll check to make sure everything is right:

$$Acetic\ Acid\ = \left(\frac{0.25}{0.9375}\right) = 0.2667M$$

$$NaOH\ = \left(\frac{0.6875 - 0.25}{0.9375}\right) = 0.4667M$$

$$5.00 = 4.756 + \log\left(\frac{[base]}{[acid]}\right)$$

$$pH = 4.756 + \log\left(\frac{[0.4667]}{[0.2667]}\right)$$

$$pH = 4.756 + 0.243 = 4.999$$

We get a pH of 4.999 which is about 5.00 and isn't exactly 5.00 due to rounding early in the problem, so the problem was done correctly.

Q51

0.15M of HBr is added into 50mL of 0.1M $Ca(OH)_2$ for the titration.

a. What is the pH of the solution before HBr is added?
b. What is the pH of the solution at the point when it needs 1 mL of HBr to neutralize the solution?
c. What is the pH of the solution when it is titrated 1 mL past neutralization?

Solution

$$2HBr + Ca(OH)_2 \rightleftharpoons 2H_2O + CaBr_2 \tag{15.E.1}$$

a) $Ca(OH)_2$ is strong base. They dissociate completely.

$$[\mathrm{OH^-}] = 2[\mathrm{Ca(OH)_2}] = 0.2\mathrm{M}$$

$$\mathrm{pH} = \mathrm{pK_w} - \mathrm{pOH}$$

$$\mathrm{pH} = 14 + \log(0.2\ \mathrm{M})$$

$$\mathrm{pH} = 13.3$$

b) Because Ca(OH)$_2$ and HBr are both strong base and strong acid, at equilibrium, the pH is 7.00.

$$\mathrm{mole_{Ca(OH)_2}} = \mathrm{(Volume)(Molarity)} \tag{15.E.2}$$

$$\mathrm{mole_{Ca(OH)_2}} = \mathrm{(0.05L)(0.1M)} \tag{15.E.3}$$

$$\mathrm{mole_{Ca(OH)_2}} = 0.005\ \mathrm{mol} \tag{15.E.4}$$

@ equilibrium;

$$\mathrm{mole_{HBr}} = 2\ \mathrm{mole_{Ca(OH)_2}} \tag{15.E.5}$$

$$\mathrm{mole_{HBr}} = 2(0.005\ \mathrm{mol}) = 0.01\ \mathrm{mol} \tag{15.E.6}$$

$$\mathrm{Volume_{HBr}} = \frac{\mathrm{mole_{HBr}}}{\mathrm{molarity_{HBr}}} = \frac{0.01\ \mathrm{mol}}{0.15\mathrm{M}} = 0.0667\ \mathrm{L} = 66.7\ \mathrm{mL} \tag{15.E.7}$$

$$\text{Total Volume at equilibrium} = 66.7\mathrm{mL} + 50\mathrm{mL} = 116.7\mathrm{mL} \tag{15.E.8}$$

$$\text{Total Volume 1mL short of equilibrium} = 116.7\mathrm{mL} - 1\mathrm{mL} = 115.7\mathrm{mL} \tag{15.E.9}$$

$$\mathrm{Volume_{HBr}}\ \text{1mL short of equilibrium} = 66.7\mathrm{mL} - 1\mathrm{mL} = 65.7\ \mathrm{mL} \tag{15.E.10}$$

$$\text{mols of } \mathrm{OH^-} \text{ not neutralized by HBr} = 0.01\ \mathrm{mol} - 0.0657\ \mathrm{L} \times (0.15\ \mathrm{M}) = 1.45 \times 10^{-4}\ \mathrm{mol} \tag{15.E.11}$$

$$\mathrm{pH} = 14 + \log\left(\frac{1.45^{-4}\ \mathrm{mol}}{0.1157\ \mathrm{L}}\right) = 11.1 \tag{15.E.12}$$

c)

At 1mL after equilibrium, Ca(OH)$_2$ has been neutralized by HBr. Only HBr exists in the solution.

$$\mathrm{mole_{HBr}} = \mathrm{(0.001L)(0.15M)} = 1.5 \times 10^{-4}\ \mathrm{mol} \tag{15.E.13}$$

$$\text{Volume} = \text{Total Volume} + 1\mathrm{mL} = 117.7\mathrm{mL} = 0.1177\ \mathrm{L} \tag{15.E.14}$$

$$\mathrm{M_{HBr}}\ \text{in the solution} = \frac{1.5 \times 10^{-4}\ \mathrm{mol}}{0.1177\ \mathrm{L}} = 1.274 \times 10^{-3}\mathrm{M} \tag{15.E.15}$$

$$\mathrm{M_{HBr}}\ \text{in the solution} = \mathrm{M_{H^+}}\ \text{in the solution} \tag{15.E.16}$$

$$\mathrm{pH} = -\log[\mathrm{H^+}] = -\log(1.274 \times 10^{-3}\mathrm{M}) = 2.89 \tag{15.E.17}$$

Q55

K$_b$ at 25°C for Diethylamine ($(\mathrm{(C_2H_5)_2NH})$) is 1.3×10^{-3}. Consider the titration of 50.00 mL of a 0.1000 M solution of Diethylamine with 0.100 M HCl added with the following volumes: 0, 10.00, 50.00 mL. Calculate pH for each solutions. At an unknown volume beyond 50.00 mL, the pH is 3.90. Find the corresponding amount volume of HCl needed to obtain that pH.

Solution

When HCl volume = 0.00 mL.

$$DiEtNH_{(aq)} + H_2O_{(l)} \rightleftharpoons DiEtNH^+_{2(aq)} + OH^-_{aq} \tag{15.E.18}$$

$$\frac{[DiEtNH_2^+][OH^-]}{[DiEtNH]} = 1.3 \times 10^{-3} \tag{15.E.19}$$

$$[OH^-] = [DiEtNH_2^+] = y$$

$$[DiEtNH] = 0.1000 - y$$

$$\frac{y^2}{0.1000-y} = 1.3\times10^{-3} \tag{15.E.20}$$

$$\mathrm{y = 0.01077M = [OH^-]}$$

$$\mathrm{pOH = 1.97}$$

$$\mathrm{pH = 12.03}$$

When HCl volume = 10.00 mL.

$$\mathrm{[DiEtNH_2^+] = \frac{(0.1000M)(0.01L)}{(0.050+0.010)L} = 0.0167\ M} \tag{15.E.21}$$

$$\mathrm{[DiEtNH] = \frac{(0.1000M(0.050L)-(0.1000M)(0.01L)}{(0.050+0.010)L} = 0.0667\ M} \tag{15.E.22}$$

Plug it back to Henerson Hasselbalch equation

$$\mathrm{pOH = pK_b + \log(\frac{[BH^+]}{[B]})} \tag{15.E.23}$$

\[\mathrm{pOH = -\log(1.3 \times 10^{-3}) +\log(\dfrac{[0.0167 \; M]}{[0.0667 \; M]})}$$

$$\mathrm{pH = pH - pOH = 14.00 - 2.28 = 11.72} \tag{15.E.24}$$

When HCl volume = 50 mL.

The titration is at the equivalence point. At equivalence, the reaction consists of 100 mL of 0.050 mol $\mathrm{DiEtNH_2^+}$

$$\mathrm{DiEtNH^+_{2(aq)} + H_2O_{(l)} \rightleftharpoons DiEtNH_{(aq)} + H_3O^+_{(aq)}} \tag{15.E.25}$$

$$\mathrm{K_a = \frac{1.00\times10^{-14}}{1.3\times10^{-3}} = 7.69\times10^{-12}}$$

$$\mathrm{K_a = 7.69\times10^{-12} = \frac{x^2}{(0.5000-x)}; x = [H_3O^+]} \tag{15.E.26}$$

$$\mathrm{x = 1.96\times10^{-6}; pH = 5.71}$$

Beyond the equivalence point

Beyond the equivalence point, solution behaves like HCl.

Given pH = 3.90.

$$\mathrm{10^{-3.90} = \frac{(z-0.050\ L)}{0.100\ L + z}\times 0.1000\ M} \tag{15.E.27}$$

$\mathrm{z = 0.0502\ L}$

Q57

Sodium Bicarbonate ($\mathrm{NaHCO_3}$) is a very weak base when dissolved in water. Some amount of sodium bicarbonate is dissolved in 125 mL of a 0.25 M solution of $\mathrm{HNO_3}$. The 168 mL of 0.15 M NaOH was used to titrate the solution. How many grams of sodium bicarbonate were added?

Solution

We are titrating an acid with two bases so solve for the amount of acid the NaOH neutralizes and the remaining moles of acid will be the number of moles of sodium bicarbonate.

$$\mathrm{Moles\ HNO_3 = \frac{0.25\ moles}{1\ L}\times 0.125\ L = 0.03125\ moles}$$

$$\text{Moles NaOH} = \frac{0.15 \text{ moles}}{1 \text{ L}} \times 0.168 \text{ L} = 0.0252 \text{ moles}$$

$$0.03125 - 0.0252 = 0.00605 \text{ moles sodium bicarbonate}$$

Now just multiply by sodium bicarbonate's molar mass (84.007 $\frac{g}{mol}$) to find the mass of sodium bicarbonate added

$$0.00605 \times 84.007 = 0.51\text{g}$$

Q59

What is the molarity of a HNO_3 water solution if it requires 31.80 mL of such solution to titrate 0.0662 g Aniline in 100 mL aqueous solution to equivalence point? What will the pH value be at the equivalence point if $\text{K}_\text{b}(\text{Aniline}) = 3.8 \times 10^{-10}$?

Solution

Aniline and HNO_3 react with a one-to-one stoichiometry

$$\text{C}_6\text{H}_5\text{NH}_2(\text{aq}) + \text{HNO}_3(\text{aq}) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+(\text{aq}) + \text{NO}_3^-(\text{aq})$$

Therefore

$$M(HNO_3) = \frac{0.0662\ g}{93.13\ g/mol} \times \frac{1}{0.03180\ L} = 0.0224\ M$$

Suppose at the equivalence point all Aniline is converted to its conjugate acid, then its concentration equals

$$[\text{C}_6\text{H}_5\text{NH}_3^+] = \frac{0.0662\, g}{(93.13\, g/mol)\ 0.1318\, L} = 0.00539\, M$$

Also as some Aniline's conjugate acid reacts with water,

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{3.8 \times 10^{-10}} = 2.63 \times 10^{-5} = \frac{[H_3O^+][C_6H_5NH_2]}{[C_6H_5NH_3^+]} = \frac{x^2}{0.00539 - x}$$

Therefore,

$$x = [H_3O^+] = 3.636 \times 10^{-4} M$$

so $\text{pH} = 3.44$.

CHAPTER OVERVIEW

16: Solubility and Precipitation Equilibria

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI
XVII XVIII XIX XX XXI XXII XXIII • **Homework Exercises**

Template:HideTOC

Solubility equilibrium is a type of dynamic equilibrium. It exists when a chemical compound in the solid state is in chemical equilibrium with a solution of that compound. The solid may dissolve unchanged, with dissociation or with chemical reaction with another constituent of the solvent, such as acid or alkali. Each type of equilibrium is characterized by a temperature-dependent equilibrium constant. Solubility equilibria are important in pharmaceutical, environmental and many other scenarios.

16.1: The Nature of Solubility Equilibria

Learning Objectives

- Understand the qualitative nature of dissolving a salt in water

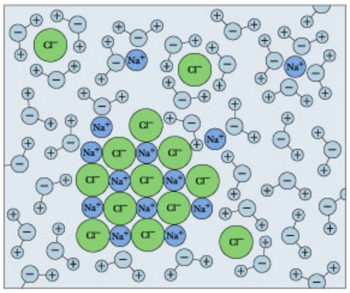
Dissolution of a salt in water is a chemical process that is governed by the same laws of chemical equilibrium that apply to any other reaction. There are, however, a number of special aspects of of these equilibria that set them somewhat apart from the more general ones that are covered in the lesson set devoted specifically to chemical equilibrium. These include such topics as the common ion effect, the influence of pH on solubility, supersaturation, and some special characteristics of particularly important solubility systems... all explained in what follows.

The Dissolution of Salts in Water

Drop some ordinary table salt into a glass of water, and watch it "disappear". We refer to this as *dissolution*, and we explain it as a process in which the sodium and chlorine units break away from the crystal surface, get surrounded by H_2O molecules, and become *hydrated ions*.

$$\mathrm{NaCl(s)} \rightarrow \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)}$$

The designation *(aq)* means "aqueous" and comes from *aqua*, the Latin word for water. It is used whenever we want to emphasize that the ions are hydrated — that H_2O molecules are attached to them.



Remember that solubility equilibrium and the calculations that relate to it are only meaningful when *both* sides (solids and dissolved ions) are simultaneously present. But if you keep adding salt, there will come a point at which it no longer seems to dissolve. If this condition persists, we say that the salt has reached its *solubility limit*, and the solution is *saturated* in NaCl. The situation is now described by

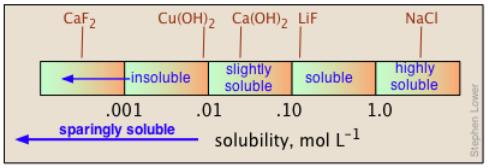
$$\mathrm{NaCl(s)} \rightleftharpoons \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)}$$

in which the solid and its ions are *in equilibrium*.

Salt solutions that have reached or exceeded their solubility limits (usually 36-39 g per 100 mL of water) are responsible for prominent features of the earth's geochemistry. They typically form when NaCl leaches from soils into waters that flow into salt lakes in arid regions that have no natural outlets; subsequent evaporation of these brines force the above equilibrium to the left, forming natural salt deposits. These are often admixed with other salts, but in some cases are almost pure NaCl. Many parts of the world contain buried deposits of NaCl (known as halite) that formed from the evaporation of ancient seas, and which are now mined.

Expressing solubilities

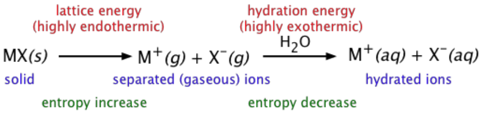
Solubilities are most fundamentally expressed in molar (mol L^{-1} of solution) or molal (mol kg^{-1} of water) units. But for practical use in preparing stock solutions, chemistry handbooks usually express solubilities in terms of grams-per-100 ml of water at a given temperature, frequently noting the latter in a superscript. Thus 6.9^{20} means 6.9 g of solute will dissolve in 100 mL of water at 20° C.



When quantitative data are lacking, the designations "soluble", "insoluble", "slightly soluble", and "highly soluble" are used. There is no agreed-on standard for these classifications, but a useful guideline might be that shown below.

What determines solubility?

The solubilities of salts in water span a remarkably large range of values, from almost completely insoluble to highly soluble. Moreover, there is no simple way of predicting these values, or even of explaining the trends that are observed for the solubilities of different anions within a given group of the periodic table.



Ultimately, the driving force for dissolution (and for *all* chemical processes) is determined by the Gibbs free energy change. Dissolution of a salt is conceptually understood as a sequence of the two processes depicted above:

1. breakup of the ionic lattice of the solid (i.e., lattice energy)
2. followed by attachment of water molecules to the released ions (Solvation or Hydration Energy).

The first step consumes a large quantity of energy, something that by itself would strongly discourage solubility. But the second step *releases* a large amount of energy and thus has the opposite effect. Thus the net energy change depends on the sum of two large energy terms (often approaching 1000 kJ/mol) having opposite signs. Each of these terms will to some extent be influenced by the size, charge, and polarizability of the particular ions involved, and on the lattice structure of the solid. This large number of variables makes it impossible to predict the solubility of a given salt.

Nevertheless, there are some clear trends for how the solubilities of a series of salts of a given anion (such as hydroxides, sulfates, etc.) change with a periodic table group. And of course, there are a number of general *solubility rules*.

Solubility Rules

1. Salts containing Group I elements are soluble (Li^+, Na^+, K^+, Cs^+, Rb^+). Exceptions to this rule are rare. Salts containing the ammonium ion (NH_4^+) are also soluble.
2. Salts containing nitrate ion (NO_3^-) are generally soluble.
3. Salts containing Cl^-, Br^-, I^- are generally soluble. Important exceptions to this rule are halide salts of Ag^+, Pb^{2+}, and $(Hg_2)^{2+}$. Thus, $AgCl$, $PbBr_2$, and Hg_2Cl_2 are all insoluble.
4. Most silver salts are insoluble. $AgNO_3$ and $Ag(C_2H_3O_2)$ are common soluble salts of silver; virtually anything else is insoluble.
5. Most sulfate salts are soluble. Important exceptions to this rule include $BaSO_4$, $PbSO_4$, Ag_2SO_4 and $SrSO_4$.
6. Most hydroxide salts are only slightly soluble. Hydroxide salts of Group I elements are soluble. Hydroxide salts of Group II elements (Ca, Sr, and Ba) are slightly soluble. Hydroxide salts of transition metals and Al^{3+} are insoluble. Thus, $Fe(OH)_3$, $Al(OH)_3$, $Co(OH)_2$ are not soluble.
7. Most sulfides of transition metals are highly insoluble. Thus, CdS, FeS, ZnS, Ag_2S are all insoluble. Arsenic, antimony, bismuth, and lead sulfides are also insoluble.
8. Carbonates are frequently insoluble. Group II carbonates (Ca, Sr, and Ba) are insoluble. Some other insoluble carbonates include $FeCO_3$ and $PbCO_3$.
9. Chromates are frequently insoluble. Examples: $PbCrO_4$, $BaCrO_4$
10. Phosphates are frequently insoluble. Examples: $Ca_3(PO_4)_2$, Ag_3PO_4
11. Fluorides are frequently insoluble. Examples: BaF_2, MgF_2 PbF_2.

A solution must be saturated to be in equilibrium with the solid. This is a *necessary* condition for solubility equilibrium, but it is not by itself *sufficient*. True chemical equilibrium can only occur when all components are simultaneously present. A solubility system can be in equilibrium only when some of the solid is in contact with a saturated solution of its ions. Failure to appreciate this is a very common cause of errors in solving solubility problems.

Undersaturated and supersaturated solutions

If the ion product is smaller than the solubility product, the system is not in equilibrium and no solid can be present. Such a solution is said to be *undersaturated*. A *supersaturated* solution is one in which the ion product exceeds the solubility product. A supersaturated solution is not at equilibrium, and no solid can ordinarily be present in such a solution. If some of the solid is added, the excess ions precipitate out and until solubility equilibrium is achieved.

Solubility and Temperature

Solubility usually increases with temperature - but not always. This is very apparent from the solubility-vs.-temperature plots shown in Figure 16.1.1. (Some of the plots are colored differently in order to make it easier to distinguish them where they crowd together.) The temperature dependence of any process depends on its entropy change — that is, on the degree to which thermal kinetic energy can spread throughout the system. When a solid dissolves, its component molecules or ions diffuse into the much greater volume of the solution, carrying their thermal energy along with them. So we would normally expect the entropy to increase — something that makes any process take place to a greater extent at a higher temperature.

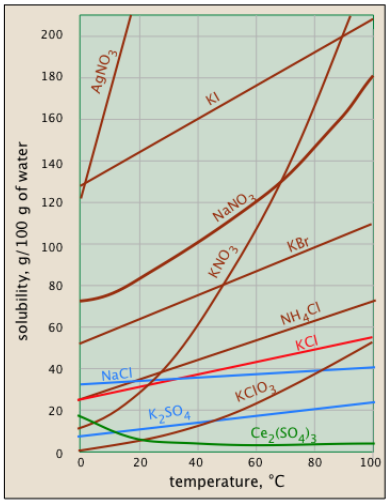


Figure 16.1.1: Solubility of select salts in water as a function of temperature.

So why does the solubility of cerium sulfate (green plot) diminish with temperature? Dispersal of the Ce^{3+} and SO_4^{2-} ions themselves is still associated with an entropy increase, but in this case the entropy of the *water*decreases even more owing to the ordering of the H_2O molecules that attach to the Ce^{3+} ions as they become hydrated. It's difficult to predict these effects, or explain why they occur in individual cases — but they do happen.

Contributors and Attributions

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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16.2: Ionic Equilibria between Solids and Solutions

Learning Objectives

- To calculate the solubility of an ionic compound from its K_{sp}

We begin our discussion of solubility and complexation equilibria—those associated with the formation of complex ions—by developing quantitative methods for describing dissolution and precipitation reactions of ionic compounds in aqueous solution. Just as with acid–base equilibria, we can describe the concentrations of ions in equilibrium with an ionic solid using an equilibrium constant expression.

The Solubility Product

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)} \tag{16.2.1}$$

As you will discover in more advanced chemistry courses, basic anions, such as S^{2-}, $PO_4{}^{3-}$, and $CO_3{}^{2-}$, react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate.

The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2}{[\mathrm{Ca_3(PO_4)_2}]} \tag{16.2.2}$$

$$[\mathrm{Ca_3(PO_4)_2}]K = K_{\mathrm{sp}} = [\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2 \tag{16.2.3}$$

At 25°C and pH 7.00, Ksp for calcium phosphate is 2.07×10^{-33}, indicating that the concentrations of Ca^{2+} and $PO_4{}^{3-}$ ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts are listed in Table 16.2.1, which shows that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH in Equations 16.2.2 and 16.2.3, changes in pH can affect the solubility of a compound as discussed later.

> *As with K, the concentration of a pure solid does not appear explicitly in K_{sp}.*

Table 16.2.1: Solubility Products for Selected Ionic Substances at 25°C

Solid	Color	Ksp	Solid	Color	Ksp
Acetates			**Iodides**		
$Ca(O_2CCH_3)_2·3H_2O$	white	4×10^{-3}	Hg_2I_2*	yellow	5.2×10^{-29}
Bromides			PbI_2	yellow	9.8×10^{-9}
AgBr	off-white	5.35×10^{-13}	**Oxalates**		
Hg_2Br_2*	yellow	6.40×10^{-23}	$Ag_2C_2O_4$	white	5.40×10^{-12}
Carbonates			$MgC_2O_4·2H_2O$	white	4.83×10^{-6}
$CaCO_3$	white	3.36×10^{-9}	PbC_2O_4	white	4.8×10^{-10}
$PbCO_3$	white	7.40×10^{-14}	**Phosphates**		

*These contain the $Hg_2{}^{2+}$ ion.

Solid	Color	Ksp	Solid	Color	Ksp
Chlorides			Ag_3PO_4	white	8.89×10^{-17}
AgCl	white	1.77×10^{-10}	$Sr_3(PO_4)_2$	white	4.0×10^{-28}
Hg_2Cl_2*	white	1.43×10^{-18}	$FePO_4 \cdot 2H_2O$	pink	9.91×10^{-16}
$PbCl_2$	white	1.70×10^{-5}	**Sulfates**		
Chromates			Ag_2SO_4	white	1.20×10^{-5}
$CaCrO_4$	yellow	7.1×10^{-4}	$BaSO_4$	white	1.08×10^{-10}
$PbCrO_4$	yellow	2.8×10^{-13}	$PbSO_4$	white	2.53×10^{-8}
Fluorides			**Sulfides**		
BaF_2	white	1.84×10^{-7}	Ag_2S	black	6.3×10^{-50}
PbF_2	white	3.3×10^{-8}	CdS	yellow	8.0×10^{-27}
Hydroxides			PbS	black	8.0×10^{-28}
$Ca(OH)_2$	white	5.02×10^{-6}	ZnS	white	1.6×10^{-24}
$Cu(OH)_2$	pale blue	1×10^{-14}			
$Mn(OH)_2$	light pink	1.9×10^{-13}			
$Cr(OH)_3$	gray-green	6.3×10^{-31}			
$Fe(OH)_3$	rust red	2.79×10^{-39}			
*These contain the Hg_2^{2+} ion.					

Solubility products are determined experimentally by directly measuring either the concentration of one of the component ions or the solubility of the compound in a given amount of water. However, whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp}, like K, is defined in terms of the molar concentrations of the component ions.

A color photograph of a kidney stone, 8 mm in length. Kidney stones form from sparingly soluble calcium salts and are largely composed of $Ca(O_2CCO_2) \cdot H_2O$ *and* $Ca_3(PO_4)_2$*. from Wikipedia.*

✓ Example 16.2.1: Kidney Stones

Calcium oxalate monohydrate $[Ca(O_2CCO_2) \cdot H_2O$, also written as $CaC_2O_4 \cdot H_2O]$ is a sparingly soluble salt that is the other major component of kidney stones [along with $Ca_3(PO_4)_2$]. Its solubility in water at 25°C is 7.36×10^{-4} g/100 mL. Calculate its K_{sp}.

Given: solubility in g/100 mL

Asked for: K_{sp}

Strategy:

A. Write the balanced dissolution equilibrium and the corresponding solubility product expression.
B. Convert the solubility of the salt to moles per liter. From the balanced dissolution equilibrium, determine the equilibrium concentrations of the dissolved solute ions. Substitute these values into the solubility product expression to calculate K_{sp}.

Solution

A We need to write the solubility product expression in terms of the concentrations of the component ions. For calcium oxalate monohydrate, the balanced dissolution equilibrium and the solubility product expression (abbreviating oxalate as ox^{2-}) are as follows:

$$\mathrm{Ca(O_2CCO_2)\cdot H_2O(s) \rightleftharpoons Ca^{2+}(aq) + {}^-O_2CCO_2^-(aq) + H_2O(l)} \quad K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{ox^{2-}}]$$

Neither solid calcium oxalate monohydrate nor water appears in the solubility product expression because their concentrations are essentially constant.

B Next we need to determine $[Ca^{2+}]$ and $[ox^{2-}]$ at equilibrium. We can use the mass of calcium oxalate monohydrate that dissolves in 100 mL of water to calculate the number of moles that dissolve in 100 mL of water. From this we can determine the number of moles that dissolve in 1.00 L of water. For dilute solutions, the density of the solution is nearly the same as that of water, so dissolving the salt in 1.00 L of water gives essentially 1.00 L of solution. Because each 1 mol of dissolved calcium oxalate monohydrate dissociates to produce 1 mol of calcium ions and 1 mol of oxalate ions, we can obtain the equilibrium concentrations that must be inserted into the solubility product expression. The number of moles of calcium oxalate monohydrate that dissolve in 100 mL of water is as follows:

$$\frac{7.36\times10^{-4}\ \mathrm{g}}{146.1\ \mathrm{g/mol}} = 5.04\times10^{-6}\ \mathrm{mol\ Ca(O_2CCO_2)\cdot H_2O}$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$\left(\frac{5.04\times10^{-6}\ \mathrm{mol\ Ca(O_2CCO_2\cdot)H_2O}}{100\ \mathrm{mL}}\right)\left(\frac{1000\ \mathrm{mL}}{1.00\ \mathrm{L}}\right) = 5.04\times10^{-5}\ \mathrm{mol/L} = 5.04\times10^{-5}\ \mathrm{M}$$

Because of the stoichiometry of the reaction, the concentration of Ca^{2+} and ox^{2-} ions are both 5.04×10^{-5} M. Inserting these values into the solubility product expression,

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (5.04\times10^{-5})(5.04\times10^{-5}) = 2.54\times10^{-9}$$

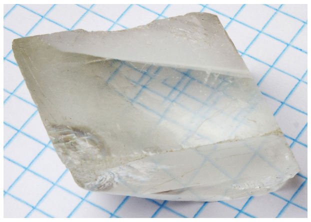
In our calculation, we have ignored the reaction of the weakly basic anion with water, which tends to make the actual solubility of many salts greater than the calculated value.

? Exercise 16.2.1

One crystalline form of calcium carbonate ($CaCO_3$) is the mineral sold as “calcite” in mineral and gem shops. The solubility of calcite in water is 0.67 mg/100 mL. Calculate its K_{sp}.

Answer 4.5×10^{-9}

> *The reaction of weakly basic anions with H_2O tends to make the actual solubility of many salts higher than predicted.*



A crystal of calcite ($CaCO_3$), illustrating the phenomenon of double refraction. When a transparent crystal of calcite is placed over a page, we see two images of the letters. Image used with permisison from Wikipedia

Calcite, a structural material for many organisms, is found in the teeth of sea urchins. The urchins create depressions in limestone that they can settle in by grinding the rock with their teeth. Limestone, however, also consists of calcite, so how can the urchins grind the rock without also grinding their teeth? Researchers have discovered that the teeth are shaped like needles and plates and contain magnesium. The concentration of magnesium increases toward the tip, which contributes to the hardness. Moreover, each tooth is composed of two blocks of the polycrystalline calcite matrix that are interleaved near the tip. This creates a corrugated surface that presumably increases grinding efficiency. Toolmakers are particularly interested in this approach to grinding.

Tabulated values of K_{sp} can also be used to estimate the solubility of a salt with a procedure that is essentially the reverse of the one used in Example 16.2.1. In this case, we treat the problem as a typical equilibrium problem and set up a table of initial concentrations, changes in concentration, and final concentrations (ICE Tables), remembering that the concentration of the pure solid is essentially constant.

✓ Example 16.2.2

We saw that the K_{sp} for $Ca_3(PO_4)_2$ is 2.07×10^{-33} at 25°C. Calculate the aqueous solubility of $Ca_3(PO_4)_2$ in terms of the following:

a. the molarity of ions produced in solution
b. the mass of salt that dissolves in 100 mL of water at 25°C

Given: K_{sp}

Asked for: molar concentration and mass of salt that dissolves in 100 mL of water

Strategy:

A. Write the balanced equilibrium equation for the dissolution reaction and construct a table showing the concentrations of the species produced in solution. Insert the appropriate values into the solubility product expression and calculate the molar solubility at 25°C.
B. Calculate the mass of solute in 100 mL of solution from the molar solubility of the salt. Assume that the volume of the solution is the same as the volume of the solvent.

Solution:

A. **A** The dissolution equilibrium for $Ca_3(PO_4)_2$ (Equation 16.2.2) is shown in the following ICE table. Because we are starting with distilled water, the initial concentration of both calcium and phosphate ions is zero. For every 1 mol of $Ca_3(PO_4)_2$ that dissolves, 3 mol of Ca^{2+} and 2 mol of PO_4^{3-} ions are produced in solution. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ will be $+3x$, and the change in $[PO_4^{3-}]$ will be $+2x$. We can insert these values into the table.

$$\mathbf{Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)}$$

	$Ca_3(PO_4)_2$	$[Ca^{2+}]$	`\ce{[PO4^{3−}}]`
initial	pure solid	0	0
change	—	$+3x$	$+2x$
final	pure solid	$3x$	$2x$

Although the amount of solid $Ca_3(PO_4)_2$ changes as some of it dissolves, its molar concentration does not change. We now insert the expressions for the equilibrium concentrations of the ions into the solubility product expression (Equation 17.2):

$$\begin{aligned} K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 &= (3x)^3(2x)^2 \\ 2.07 \times 10^{-33} &= 108x^5 \\ 1.92 \times 10^{-35} &= x^5 \\ 1.14 \times 10^{-7}\ M &= x \end{aligned}$$

This is the molar solubility of calcium phosphate at 25°C. However, the molarity of the ions is $2x$ and $3x$, which means that $[PO_4^{3-}] = 2.28 \times 10^{-7}$ and $[Ca^{2+}] = 3.42 \times 10^{-7}$.

b. **B** To find the mass of solute in 100 mL of solution, we assume that the density of this dilute solution is the same as the density of water because of the low solubility of the salt, so that 100 mL of water gives 100 mL of solution. We can then determine the amount of salt that dissolves in 100 mL of water:

$$\left(\frac{1.14 \times 10^{-7}\ \text{mol}}{1\ \text{L}}\right) 100\ \text{mL} \left(\frac{1\ \text{L}}{1000\ \text{mL}}\right) \left(\frac{310.18\ \text{g Ca}_3(\text{PO}_4)_2}{1\ \text{mol}}\right) = 3.54 \times 10^{-6}\ \text{g Ca}_3(\text{PO}_4)_2$$

? Exercise 16.2.2

The solubility product of silver carbonate (Ag_2CO_3) is 8.46×10^{-12} at 25°C. Calculate the following:

a. the molarity of a saturated solution
b. the mass of silver carbonate that will dissolve in 100 mL of water at this temperature

Answer a

1.28×10^{-4} M

Answer a

3.54 mg

Relating Solubilities to Solubility Constants

The *solubility* (by which we usually mean the *molar solubility*) of a solid is expressed as the concentration of the "dissolved solid" in a *saturated solution.* In the case of a simple 1:1 solid such as AgCl, this would just be the concentration of Ag^+ or Cl^- in the saturated solution. But for a more complicated stoichiometry such as as silver chromate, the solubility would be only one-half of the Ag^+ concentration.

For example, let us denote the solubility of Ag_2CrO_4 as S mol L^{-1}. Then for a saturated solution, we have

- $[Ag^+] = 2S$
- $[CrO_4^{2-}] = S$

Substituting this into Eq 5b above,

$$(2S)^2(S) = 4S^3 = 2.76 \times 10^{-12} \tag{16.2.4}$$

$$S = (dfracK_{sp}4)^{1/3} = (6.9 \times 10^{-13})^{1/3} = 0.88 \times 10^{-4} \tag{16.2.5}$$

thus the solubility is $8.8 \times 10^{-5}\ M$.

Note that the relation between the solubility and the solubility product constant depends on the stoichiometry of the dissolution reaction. For this reason it is meaningless to compare the solubilities of two salts having the formulas A_2B and AB_2, say, on the basis of their K_s values.

> It is *meaningless* to compare the solubilities of two salts having different formulas on the basis of their K_s values.

✓ Example 16.2.2

The solubility of CaF_2 (molar mass 78.1) at 18°C is reported to be 1.6 mg per 100 mL of water. Calculate the value of K_s under these conditions.

Solution

moles of solute in 100 mL; S = 0.0016 g / 78.1 g/mol = 2.05×10^{-5} mol

$$\begin{aligned} S &= \frac{2.05 \times 10^{-5} mol}{0.100\ L} \\ &= 2.05 \times 10^{-4} M \end{aligned}$$

$$\begin{aligned} K_{sp} &= [Ca^{2+}][F^-]^2 \\ &= (S)(2S)^2 \\ &= 4 \times (2.05 \times 10^{-4})^3 \\ &= 3.44 \times 10^{-11} \end{aligned}$$

✓ Example 16.2.3

Estimate the solubility of $La(IO_3)_3$ and calculate the concentration of iodate in equilibrium with solid lanthanum iodate, for which $K_s = 6.2 \times 10^{-12}$.

Solution

The equation for the dissolution is

$$\mathrm{La(IO_3)_3 \rightleftharpoons La^{3+} + 3\,IO_3^-}$$

If the solubility is S, then the equilibrium concentrations of the ions will be

$[La^{3+}] = S$ and $[IO_3^-] = 3S$. Then $K_s = [La^{3+}][IO_3^-]^3 = S(3S)^3 = 27S^4$

$27S^4 = 6.2 \times 10^{-12}$, $S = ((6.2 \div 27) \times 10^{-12})^{1/4} = 6.92 \times 10^{-4}$ $\underline{M}$

$[IO_3^-] = 3S = 2.08 \times 10^{-5}$ ($\underline{M}$)

✓ Example 16.2.4: Cadmium

Cadmium is a highly toxic environmental pollutant that enters wastewaters associated with zinc smelting (Cd and Zn commonly occur together in ZnS ores) and in some electroplating processes. One way of controlling cadmium in effluent streams is to add sodium hydroxide, which precipitates insoluble $Cd(OH)_2$ (K_s = 2.5E–14). If 1000 L of a certain wastewater contains Cd^{2+} at a concentration of 1.6E–5 $\underline{M}$, what concentration of Cd^{2+} would remain after addition of 10 L of 4 $\underline{M}$ NaOH solution?

Solution

As with most real-world problems, this is best approached as a series of smaller problems, making simplifying approximations as appropriate.

Volume of treated water: 1000 L + 10 L = 1010 L

Concentration of OH^- on addition to 1000 L of pure water:

(4 $\underline{M}$) × (10 L)/(1010 L) = 0.040 $\underline{M}$

Initial concentration of Cd^{2+} in 1010 L of water:

$$(1.6 \times 10^{-5}\ M)\left(\frac{100}{101}\right) \approx 1.6 \times 10^{-5}\ M \tag{16.2.6}$$

The easiest way to tackle this is to start by assuming that a stoichiometric quantity of $Cd(OH)_2$ is formed — that is, *all* of the Cd^{2+} gets precipitated.

Concentrations	$[Cd^{2+}]$, $\underline{M}$	$[OH^-]$, $\underline{M}$
initial	1.6E–5	0.04
change	–1.6E–5	–3.2E–5
final:	0	0.04 – 3.2E–5 ≈ .04

Now "turn on the equilibrium" — find the concentration of Cd^{2+} that can exist in a 0.04$\underline{M}$ OH^- solution:

Concentrations	$[Cd^{2+}]$, $\underline{M}$	$[OH^-]$, $\underline{M}$

Concentrations	$[Cd^{2+}]$, $\underline{M}$	$[OH^-]$, $\underline{M}$
initial	o	0.04
change	$+x$	$+2x$
at equilibrium	x	$.04 + 2x \approx .04$

Substitute these values into the solubility product expression:

$$Cd(OH)_2(s) = [Cd^{2+}]\,[OH^-]^2 = 2.5E–14$$

$$[Cd^{2+}] = (2.5E–14) / (16E–4) = 1.6E–13\ \underline{M}$$

Note that the effluent will now be very alkaline:

$$pH = 14 + log 0.04 = 12.6 \tag{16.2.7}$$

so in order to meet environmental standards an equivalent quantity of strong acid must be added to neutralize the water before it is released.

Summary

The solubility product (K_{sp}) is used to calculate equilibrium concentrations of the ions in solution, whereas the ion product (Q) describes concentrations that are not necessarily at equilibrium. The equilibrium constant for a dissolution reaction, called the solubility product (K_{sp}), is a measure of the solubility of a compound. Whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp} is defined in terms of the molar concentrations of the component ions.

16.3: Precipitation and the Solubility Product

Learning Objectives

- Define K_{sp}, the solubility product.
- Explain solid/solution equilibria using K_{sp} and Q_{sp}.
- Calculate molarity of saturated solution from K_{sp}.
- Calculate K_{sp} from molarity of saturated solution.

Precipitation reactions occur when cations and anions in aqueous solution combine to form an insoluble ionic solid called a **precipitate**. Whether or not such a reaction occurs can be determined by using the **solubility rules** for common ionic solids. Because not all aqueous reactions form precipitates, one must consult the solubility rules before determining the state of the products and writing a **net ionic equation.** The ability to predict these reactions allows scientists to determine which ions are present in a solution, and allows industries to form chemicals by extracting components from these reactions.

Properties of Precipitates

Precipitates are insoluble ionic solid products of a reaction, formed when certain cations and anions combine in an aqueous solution. The determining factors of the formation of a precipitate can vary. Some reactions depend on temperature, such as solutions used for buffers, whereas others are dependent only on solution concentration. The solids produced in precipitate reactions are crystalline solids, and can be suspended throughout the liquid or fall to the bottom of the solution. The remaining fluid is called **supernatant liquid** (or just the supernate). The two components of the mixture (precipitate and supernate) can be separated by various methods, such as filtration, centrifuging, or decanting.

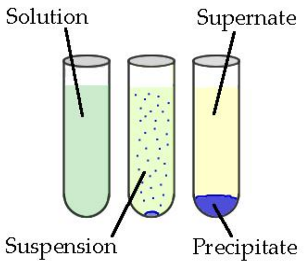


Figure 16.3.1: Above is a diagram of the formation of a precipitate in solution. (Public Domain; ZabMilenko)

The use of solubility rules require an understanding of the way that ions react. Most precipitation reactions are single replacement reactions or double replacement reactions. A double replacement reaction occurs when two ionic reactants dissociate and bond with the respective anion or cation from the other reactant. The ions replace each other based on their charges as either a cation or an anion. This can be thought of as a double displacement reaction where the partners "switching; that is, the two reactants each "lose" their partner and form a bond with a different partner:

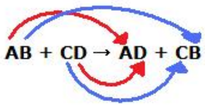


Figure 16.3.2: A double replacement reaction

A double replacement reaction is specifically classified as a **precipitation reaction** when the chemical equation in question occurs in aqueous solution and one of the of the products formed is insoluble. An example of a precipitation reaction is given below:

$$\mathrm{CdSO_4(aq) + K_2S(aq) \rightarrow CdS(s) + K_2SO_4(aq)} \tag{16.3.1}$$

Both reactants are aqueous and one product is solid. Because the reactants are ionic and aqueous, they dissociate and are therefore **soluble**. However, there are six solubility guidelines used to predict which molecules are insoluble in water. These molecules form a solid precipitate in solution.

Solubility Rules

Whether or not a reaction forms a precipitate is dictated by the solubility rules. These rules provide guidelines that tell which ions form solids and which remain in their ionic form in aqueous solution. The rules are to be followed from the top down, meaning that if something is insoluble (or soluble) due to rule 1, it has precedence over a higher-numbered rule.

1. Salts formed with group 1 cations and NH_4^+ cations are **soluble**. There are some exceptions for certain Li^+ salts.
2. Acetates ($C_2H_3O_2^-$), nitrates (NO_3^-), and perchlorates (ClO_4^-) are **soluble.**
3. Bromides, chlorides, and iodides are **soluble.**
4. Sulfates (SO_4^{2-}) are **soluble** with the exception of sulfates formed with Ca^{2+}, Sr^{2+}, and Ba^{2+}.
5. Salts containing silver, lead, and mercury (I) are **insoluble.**
6. Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), sulfides, oxides, and hydroxides (OH^-) are **insoluble**. Sulfides formed with group 2 cations and hydroxides formed with calcium, strontium, and barium are exceptions.

If the rules state that an ion is soluble, then it remains in its aqueous ion form. If an ion is insoluble based on the solubility rules, then it forms a solid with an ion from the other reactant. If all the ions in a reaction are shown to be soluble, then no precipitation reaction occurs.

Net Ionic Equations

To understand the definition of a **net ionic equation**, recall the equation for the double replacement reaction. Because this particular reaction is a precipitation reaction, states of matter can be assigned to each variable pair:

$$AB(aq) + CD(aq) \rightarrow AD(aq) + CB(s) \tag{16.3.2}$$

The first step to writing a net ionic equation is to separate the soluble (aqueous) reactants and products into their respective cations and anions. Precipitates do not dissociate in water, so the solid should not be separated. The resulting equation looks like that below:

$$A^+(aq) + B^-(aq) + C^+(aq) + D^-(aq) \rightarrow A^+(aq) + D^-(aq) + CB(s) \tag{16.3.3}$$

In the equation above, **A^+** and **D^-** ions are present on both sides of the equation. These are called **spectator ions** because they remain unchanged throughout the reaction. Since they go through the equation unchanged, they can be eliminated to show the **net ionic equation**:

$$B^-(aq) + C^+(aq) \rightarrow +CB(s) \tag{16.3.4}$$

The net ionic equation only shows the precipitation reaction. A net ionic equation must be balanced on both sides not only in terms of atoms of elements, but also in terms of electric charge. Precipitation reactions are usually represented solely by net ionic equations. If all products are aqueous, a net ionic equation cannot be written because all ions are canceled out as spectator ions. Therefore, **no precipitation reaction occurs**

Equilibrium and non-Equilibrium Conditions

The **ion product (Q)** of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (Q) discussed for gaseous equilibria. Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are not necessarily equilibrium concentrations. An ion product can in principle have *any* positive value, depending on the concentrations of the ions involved. Only in the special case when its value is identical with K_s does it become the solubility product. A solution in which this is the case is said to be *saturated*. Thus when

$$[Ag^+]^2\ [CrO_4^{2-}] = 2.76 \times 10^{-12} \tag{16.3.5}$$

at the temperature and pressure at which this value K_{sp} of applies, we say that the "solution is saturated in silver chromate".

> The ion product Q is analogous to the reaction quotient Q for gaseous equilibria.

As summarized in Figure $16.3.3$, there are three possible conditions for an aqueous solution of an ionic solid:

- $Q < K_{sp}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
- $Q = K_{sp}$. The solution is saturated and at equilibrium.
- $Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

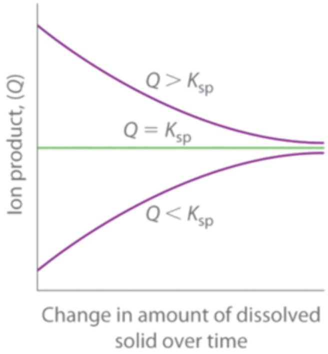


Figure 16.3.3: The Relationship between Q and K_{sp}. If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium (Q = K_{sp}). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until Q = K_{sp}. If Q = K_{sp}, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur. (CC BY-SA-NC; Anonymous)

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

✓ Example 16.3.3: barium milkshakes

Barium sulfate is used in medical imaging of the gastrointestinal tract. Its solubility product is 1.08×10^{-10} at 25°C, so it is ideally suited for this purpose because of its low solubility when a “barium milkshake” is consumed by a patient. The pathway of the sparingly soluble salt can be easily monitored by x-rays. Will barium sulfate precipitate if 10.0 mL of 0.0020 M Na_2SO_4 is added to 100 mL of 3.2×10^{-4} M $BaCl_2$? Recall that NaCl is highly soluble in water.

Given: K_{sp} and volumes and concentrations of reactants

Asked for: whether precipitate will form

Strategy:

A. Write the balanced equilibrium equation for the precipitation reaction and the expression for K_{sp}.
B. Determine the concentrations of all ions in solution when the solutions are mixed and use them to calculate the ion product (Q).
C. Compare the values of Q and K_{sp} to decide whether a precipitate will form.

Solution

A The only slightly soluble salt that can be formed when these two solutions are mixed is $\mathrm{BaSO_4}$ because NaCl is highly soluble. The equation for the precipitation of $\mathrm{BaSO_4}$ is as follows:

$$\mathrm{BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)}$$

The solubility product expression is as follows:

$$K_{sp} = [\mathrm{Ba^{2+}}][\mathrm{SO_4^{2-}}] = 1.08 \times 10^{-10}$$

B To solve this problem, we must first calculate the ion product:

$$Q = [\mathrm{Ba^{2+}}][\mathrm{SO_4^{2-}}]$$

using the concentrations of the ions that are present after the solutions are mixed and before any reaction occurs. The concentration of Ba^{2+} when the solutions are mixed is the total number of moles of Ba^{2+} in the original 100 mL of $\mathrm{BaCl_2}$ solution divided by the final volume (100 mL + 10.0 mL = 110 mL):

$$\text{moles Ba}^{2+} = 100\text{ mL}\left(\frac{1\text{ L}}{1000\text{ mL}}\right)\left(\frac{3.2\times10^{-4}\text{ mol}}{1\text{ L}}\right) = 3.2\times10^{-5}\text{ mol Ba}^{2+}$$

$$[\text{Ba}^{2+}] = \left(\frac{3.2\times10^{-5}\text{ mol Ba}^{2+}}{110\text{ mL}}\right)\left(\frac{1000\text{ mL}}{1\text{ L}}\right) = 2.9\times10^{-4}\text{ M Ba}^{2+}$$

Similarly, the concentration of SO_4^{2-} after mixing is the total number of moles of SO_4^{2-} in the original 10.0 mL of Na_2SO_4 solution divided by the final volume (110 mL):

$$\text{moles SO}_4^{2-} = 10.0\text{ mL}\left(\frac{1\text{ L}}{1000\text{ mL}}\right)\left(\frac{0.0020\text{ mol}}{1\text{ L}}\right) = 2.0\times10^{-5}\text{ mol SO}_4^{2-}$$

$$[\text{SO}_4^{2-}] = \left(\frac{2.0\times10^{-5}\text{ mol SO}_4^{2-}}{110\text{ mL}}\right)\left(\frac{1000\text{ mL}}{1\text{ L}}\right) = 1.8\times10^{-4}\text{ M SO}_4^{2-}$$

We can now calculate \(Q\):

$$Q = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (2.9\times10^{-4})(1.8\times10^{-4}) = 5.2\times10^{-8}$$

C We now compare Q with the K_{sp}. If $Q > K_{sp}$, then $BaSO_4$ will precipitate, but if $Q < K_{sp}$, it will not. Because $Q > K_{sp}$, we predict that $BaSO_4$ will precipitate when the two solutions are mixed. In fact, $BaSO_4$ will continue to precipitate until the system reaches equilibrium, which occurs when

$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = K_{sp} = 1.08\times10^{-10}.$$

Exercise 16.3.3

The solubility product of calcium fluoride (CaF_2) is 3.45×10^{-11}. If 2.0 mL of a 0.10 M solution of NaF is added to 128 mL of a $2.0\times10^{-5}\,M$ solution of $Ca(NO_3)_2$, will CaF_2 precipitate?

Answer

Yes, since $Q_{sp} = 4.7\times10^{-11} > K_{sp}$.

A solution must be saturated to be in equilibrium with the solid. This is a *necessary* condition for solubility equilibrium, but it is not by itself *sufficient*. True chemical equilibrium can only occur when all components are simultaneously present. A solubility system can be in equilibrium only when some of the solid is in contact with a saturated solution of its ions. Failure to appreciate this is a very common cause of errors in solving solubility problems.

Undersaturated and supersaturated solutions

If the ion product is smaller than the solubility product, the system is not in equilibrium and no solid can be present. Such a solution is said to be *undersaturated*. A *supersaturated* solution is one in which the ion product exceeds the solubility product. A supersaturated solution is not at equilibrium, and no solid can ordinarily be present in such a solution. If some of the solid is added, the excess ions precipitate out and until solubility equilibrium is achieved.

How to know the saturation status of a solution? Just comparing the ion product Q_s with the solubility product K_{sp}. as shown in Table 16.3.1.

Table 16.3.1: relationship among Q_{sp}, K_{sp} and saturation

Q_{sp}/K_{sp}	Status
> 1	Product concentration too high for equilibrium; net reaction proceeds to **left**.
= 1	System is at equilibrium; **no net change** will occur.
< 1	Product concentration too low for equilibrium; net reaction proceeds to **right**.

For example, for the system

$$\mathrm{Ag_2CrO_4(s) \rightleftharpoons 2\,Ag^+ + CrO_4^{2-}} \tag{16.3.6}$$

a solution in which $Q_s < K_s$ (i.e., $K_s/Q_s > 1$) is undersaturated (blue shading) and the no solid will be present. The combinations of $[\mathrm{Ag^+}]$ and $[\mathrm{CrO_4^{2-}}]$ that correspond to a saturated solution (and thus to equilibrium) are limited to those described by the curved line. The pink area to the right of this curve represents a supersaturated solution.

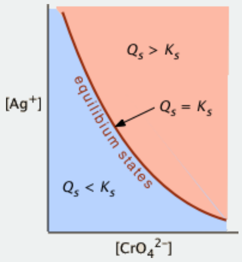


Figure 16.3.4: Equilibrium vs. non-equilibrium states for $\mathrm{Ag_2CrO_4(s)}$. (CC BY; Stephen Lower).

For some substances, formation of a solid or crystallization does not occur automatically whenever a solution is saturated. These substances have a tendency to form oversaturated solutions. For example, syrup and honey are oversaturated sugar solutions, containing other substances such as citric acids. For oversatureated solutions, Q_{sp} is greater than K_{sp}. When a seed crystal is provided or formed, a precipitate will form immediately due to equilibrium of requiring Q_{sp} to approach K_{sp}. For example Sodium acetate trihydrate, $\mathrm{NaCH_3COO \cdot 3\,H_2O}$, when heated to 370 K will become a liquid and stays as a liquid when cooled to room temperature or even below 273 K (Video 16.3.1). As soon as a seed crystal is present, crystallization occurs rapidly. In such a process, heat is released since this is an exothermic process $\Delta H < 0$.

***Video 16.3.1*:** *"hot ice" (sodium acetate) crystallized from a non-equilibrium supersaturated ($Q_{sp} > K_{sp}$) solution*

✓ Example 16.3.1

A sample of groundwater that has percolated through a layer of gypsum ($\mathrm{CaSO_4}$) with $K_{sp} = 4.9 \times 10^{-5} = 10^{-4.3}$) is found to have be $8.4 \times 10^{-5}\ M$ in $\mathrm{Ca^{2+}}$ and $7.2 \times 10^{-5}\ M$ in $\mathrm{SO_4^{2-}}$. What is the equilibrium state of this solution with respect to gypsum?

Solution

The ion product

$$Q_s = (8.4 \times 10^{-5})(7.2 \times 10^{-5}) = 6.0 \times 10^{-4}$$

exceeds K_{sp}, so the ratio $K_{sp}/Q_{sp} > 1$ and the solution is *supersaturated* in $\mathrm{CaSO_4}$.

Relating Solubilities to Solubility Constants

The *solubility* (by which we usually mean the *molar solubility*) of a solid is expressed as the concentration of the "dissolved solid" in a *saturated solution.* In the case of a simple 1:1 solid such as AgCl, this would just be the concentration of Ag^+ or $Cl^–$ in the saturated solution. But for a more complicated stoichiometry such as as silver chromate, the solubility would be only one-half of the Ag^+ concentration.

For example, let us denote the solubility of Ag_2CrO_4 as S mol L^{-1}. Then for a saturated solution, we have

- $[Ag^+] = 2S$
- $[CrO_4^{2-}] = S$

Substituting this into Eq 5b above,

$$(2S)^2(S) = 4S^3 = 2.76 \times 10^{-12} \tag{16.3.7}$$

$$S = \left(\frac{K_{sp}}{4}\right)^{1/3} = (6.9 \times 10^{-13})^{1/3} = 0.88 \times 10^{-4} \tag{16.3.8}$$

thus the solubility is $8.8 \times 10^{-5}\ M$.

Note that the relation between the solubility and the solubility product constant depends on the stoichiometry of the dissolution reaction. For this reason it is meaningless to compare the solubilities of two salts having the formulas A_2B and AB_2, say, on the basis of their K_s values.

> It is *meaningless* to compare the solubilities of two salts having different formulas on the basis of their K_s values.

Example 16.3.2

The solubility of CaF_2 (molar mass 78.1) at 18°C is reported to be 1.6 mg per 100 mL of water. Calculate the value of K_s under these conditions.

Solution

moles of solute in 100 mL; S = 0.0016 g / 78.1 g/mol = 2.05×10^{-5} mol

$$S = \frac{2.05 \times 10^{-5} mol}{0.100\ L} = 2.05 \times 10^{-4} M \tag{16.3.9}$$

$$K_{sp} = [Ca^{2+}][F^-]^2 = (S)(2S)^2 = 4 \times (2.05 \times 10^{-4})^3 = 3.44 \times 10^{-11} \tag{16.3.10}$$

Example 16.3.3

Estimate the solubility of $La(IO_3)_3$ and calculate the concentration of iodate in equilibrium with solid lanthanum iodate, for which $K_s = 6.2 \times 10^{-12}$.

Solution

The equation for the dissolution is

$$La(IO_3)_3 \rightleftharpoons La^{3+} + 3IO_3^- \tag{16.3.11}$$

If the solubility is S, then the equilibrium concentrations of the ions will be

$[La^{3+}] = S$ and $[IO_3^-] = 3S$. Then $K_s = [La^{3+}][IO_3^-]^3 = S(3S)^3 = 27S^4$

$27S^4 = 6.2 \times 10^{-12}$, $S = ((6.2 \div 27) \times 10^{-12})^{1/4} = 6.92 \times 10^{-4}$ $\underline{M}$

$[IO_3^-] = 3S = 2.08 \times 10^{-5}$ ($\underline{M}$)

Example 16.3.4: Cadmium

Cadmium is a highly toxic environmental pollutant that enters wastewaters associated with zinc smelting (Cd and Zn commonly occur together in ZnS ores) and in some electroplating processes. One way of controlling cadmium in effluent streams is to add sodium hydroxide, which precipitates insoluble $Cd(OH)_2$ (K_s = 2.5E–14). If 1000 L of a certain wastewater contains Cd^{2+} at a concentration of 1.6E–5 $\underline{M}$, what concentration of Cd^{2+} would remain after addition of 10 L of 4 $\underline{M}$ NaOH solution?

Solution

As with most real-world problems, this is best approached as a series of smaller problems, making simplifying approximations as appropriate.

Volume of treated water: 1000 L + 10 L = 1010 L

Concentration of OH^- on addition to 1000 L of pure water:

$$(4\ \underline{M}) \times (10\ \text{L})/(1010\ \text{L}) = 0.040\ \underline{M}$$

Initial concentration of Cd^{2+} in 1010 L of water:

$$(1.6 \times 10^{-5}\ M)\left(\frac{100}{101}\right) \approx 1.6 \times 10^{-5}\ M \tag{16.3.12}$$

The easiest way to tackle this is to start by assuming that a stoichiometric quantity of $Cd(OH)_2$ is formed — that is, *all* of the Cd^{2+} gets precipitated.

Concentrations	$[Cd^{2+}]$, $\boldsymbol{M}$	$[OH^-]$, $\boldsymbol{M}$
initial	1.6E–5	0.04
change	–1.6E–5	–3.2E–5
final:	0	0.04 – 3.2E–5 ≈ .04

Now "turn on the equilibrium" — find the concentration of Cd^{2+} that can exist in a 0.04$\underline{M}$ OH^- solution:

Concentrations	$[Cd^{2+}]$, $\boldsymbol{M}$	$[OH^-]$, $\boldsymbol{M}$
initial	o	0.04
change	$+x$	$+2x$
at equilibrium	x	$.04 + 2x \approx .04$

Substitute these values into the solubility product expression:

$$Cd(OH)_2(s) = [Cd^{2+}]\,[OH^-]^2 = 2.5\text{E–}14$$

$$[Cd^{2+}] = (2.5\text{E–}14) / (16\text{E–}4) = 1.6\text{E–}13\ \underline{M}$$

Note that the effluent will now be very alkaline:

$$pH = 14 + \log 0.04 = 12.6 \tag{16.3.13}$$

so in order to meet environmental standards an equivalent quantity of strong acid must be added to neutralize the water before it is released.

The Common Ion Effect

It has long been known that the solubility of a sparingly soluble ionic substance is markedly decreased in a solution of another ionic compound when the two substances have an ion in common. This is just what would be expected on the basis of the Le Chatelier Principle; whenever the process

$$CaF_{2(s)} \rightleftharpoons Ca^{2+} + 2F^- \tag{16.3.14}$$

is in equilibrium, addition of more fluoride ion (in the form of highly soluble NaF) will shift the composition to the left, reducing the concentration of Ca^{2+}, and thus effectively reducing the solubility of the solid. We can express this quantitatively by noting that the *solubility product expression*

$$[Ca^{2+}][F^-]^2 = 1.7 \times 10^{-10} \tag{16.3.15}$$

must always hold, even if some of the ionic species involved come from sources other than $CaF_2(s)$. For example, if some quantity *x* of fluoride ion is added to a solution initially in equilibrium with solid CaF_2, we have

- $[Ca^{2+}] = S$
- $[F^-] = 2S + x$

so that

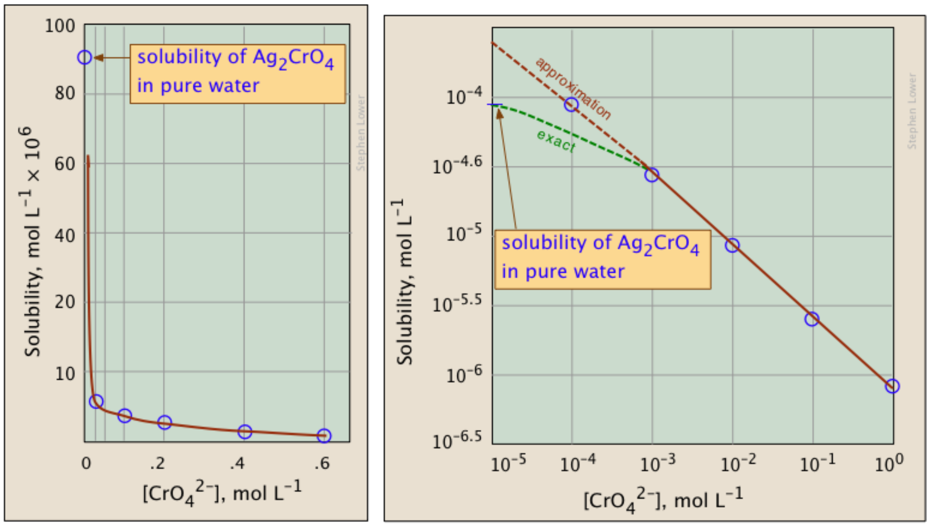
$$K_{sp} = [Ca^{2+}][F^-]^2 = S(2S + x)^2. \tag{16.3.16}$$

University-level students should be able to derive these relations for ion-derived solids of any stoichiometry. In most practical cases *x* will be large compared to *S* so that the 2*S* term can be dropped and the relation becomes

$$K_{sp} \approx S\, x^2 \tag{16.3.17}$$

$$S = \frac{K_{sp}}{x^2} \tag{16.3.18}$$

The plots shown below illustrate the common ion effect for silver chromate as the chromate ion concentration is increased by addition of a soluble chromate such as Na_2CrO_4.



What's different about the plot on the right? If you look carefully at the scales, you will see that this one is plotted logarithmically (that is, in powers of 10.) Notice how a much wider a range of values can display on a logarithmic plot. The point of showing this pair of plots is to illustrate the great utility of log-concentration plots in equilibrium calculations in which simple approximations (such as that made in Equation 16.3.18) can yield straight-lines within the range of values for which the approximation is valid.

✓ Example 16.3.5: strontium sulfate

Calculate the solubility of strontium sulfate ($K_s = 2.8 \times 10^{-7}$) in

a. pure water and
b. in a 0.10 mol L⁻¹ solution of Na_2SO_4.

Solution:

(a) In pure water, $K_s = [Sr^{2+}][SO_4^{2-}] = S^2$

$$S = \sqrt{K_s} = (2.8 \times 10^{-7})^{½} = 5.3 \times 10^{-4}$$

(b) In 0.10 mol L^{-1} Na_2SO_4, we have

$$K_s = [Sr^{2+}][SO_4^{2-}] = S \times (0.10 + S) = 2.8 \times 10^{-7}$$

Because S is negligible compared to 0.10 M, we make the approximation

$$K_s = [Sr^{2+}][SO_4^{2-}] \approx S \times (0.10\ M) = 2.8 \times 10^{-7}$$

so $S \approx (2.8 \times 10^{-7}) / 0.10M = 2.8 \times 10^{-6}$ $\underline{M}$ — which is roughly 100 times smaller than the result from *(a)*.

Note

The common ion effect usually decreases the solubility of a sparingly soluble salt.

Example 16.3.6

Calculate the solubility of calcium phosphate [$Ca_3(PO_4)_2$] in 0.20 M $CaCl_2$.

Given: concentration of $CaCl_2$ solution

Asked for: solubility of $Ca_3(PO_4)_2$ in $CaCl_2$ solution

Strategy:

A. Write the balanced equilibrium equation for the dissolution of $Ca_3(PO_4)_2$. Tabulate the concentrations of all species produced in solution.
B. Substitute the appropriate values into the expression for the solubility product and calculate the solubility of $Ca_3(PO_4)_2$.

Solution

A The balanced equilibrium equation is given in the following table. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ is once again $+3x$, and the change in $[PO_4^{3-}]$ is $+2x$. We can insert these values into the ICE table.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}(aq) + 2PO^{3-}_{4(aq)} \tag{16.3.19}$$

	$Ca_3(PO_4)_2$	$[Ca_2^+]$	$[PO_{43}-]$
initial	pure solid	0.20	0
change	—	$+3x$	$+2x$
final	pure solid	$0.20 + 3x$	$2x$

B The K_{sp} expression is as follows:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (0.20 + 3x)^3(2x)^2 = 2.07 \times 10^{-33}$$

Because $Ca_3(PO_4)_2$ is a sparingly soluble salt, we can reasonably expect that $x << 0.20$. Thus $(0.20 + 3x)$ M is approximately 0.20 M, which simplifies the K_{sp} expression as follows:

$$K_{sp} = (0.20)^3(2x)^2 = 2.07 \times 10^{-33} \tag{16.3.20}$$

$$x^2 = 6.5 \times 10^{-32} \tag{16.3.21}$$

$$x = 2.5 \times 10^{-16}\ \text{M} \tag{16.3.22}$$

This value is the solubility of $Ca_3(PO_4)_2$ in 0.20 M $CaCl_2$ at 25°C. It is approximately nine orders of magnitude less than its solubility in pure water, as we would expect based on Le Chatelier’s principle. With one exception, this example is identical to Example 16.3.2—here the initial $[Ca^{2+}]$ was 0.20 M rather than 0.

? Exercise 16.3.6

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45 × 10^{-12} at 25°C.

Answer

2.9 × 10^{-6} M (versus 1.3 × 10^{-4} M in pure water)

Applications and Examples

Precipitation reactions are useful in determining whether a certain element is present in a solution. If a precipitate is formed when a chemical reacts with lead, for example, the presence of lead in water sources could be tested by adding the chemical and monitoring for precipitate formation. In addition, precipitation reactions can be used to extract elements, such as magnesium from seawater. Precipitation reactions even occur in the human body between antibodies and antigens; however, the environment in which this occurs is still being studied.

✓ Example 16.3.7

Complete the double replacement reaction and then reduce it to the net ionic equation.

$$NaOH(aq) + MgCl_{2\ (aq)} \rightarrow$$

First, *predict the products* of this reaction using knowledge of double replacement reactions (remember the cations and anions “switch partners”).

$$2NaOH(aq) + MgCl_{2\ (aq)} \rightarrow 2NaCl + Mg(OH)_2$$

Second, *consult the solubility rules* to determine if the products are soluble. Group 1 cations (Na^+) and chlorides are soluble from rules 1 and 3 respectively, so $NaCl$ will be soluble in water. However, rule 6 states that hydroxides are insoluble, and thus $Mg(OH)_2$ will form a precipitate. The resulting equation is the following:

$$2NaOH(aq) + MgCl_{2\ (aq)} \rightarrow 2NaCl(aq) + Mg(OH)_{2\ (s)}$$

Third, *separate the reactants* into their ionic forms, as they would exist in an aqueous solution. Be sure to balance both the electrical charge and the number of atoms:

$$2Na^+(aq) + 2OH^-(aq) + Mg^{2+}(aq) + 2Cl^-(aq) \rightarrow Mg(OH)_{2\ (s)} + 2Na^+(aq) + 2Cl^-(aq)$$

Lastly, *eliminate the spectator ions* (the ions that occur on both sides of the equation unchanged). In this case, they are the sodium and chlorine ions. The final *net ionic equation* is:

$$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_{2(s)}$$

✓ Example 16.3.8

Complete the double replacement reaction and then reduce it to the net ionic equation.

$$CoCl_{2\ (aq)} + Na_2SO_{4\ (aq)} \rightarrow$$

Solution

The predicted products of this reaction are $CoSO_4$ and $NaCl$. From the solubility rules, $CoSO_4$ is soluble because rule 4 states that sulfates (SO_4^{2-}) are soluble. Similarly, we find that $NaCl$ is soluble based on rules 1 and 3. After balancing, the resulting equation is as follows:

$$CoCl_{2\ (aq)} + Na_2SO_{4\ (aq)} \rightarrow CoSO_{4\ (aq)} + 2NaCl(aq)$$

Separate the species into their ionic forms, as they would exist in an aqueous solution. Balance the charge and the atoms. Cancel out all spectator ions (those that appear as ions on both sides of the equation.):

$$\cancel{Co}^{2-}\ (aq) + \cancel{2Cl}^{-}(aq) + \cancel{2Na}^{+}\ (aq) + \cancel{SO_4}^{2-}(aq) \rightarrow \cancel{Co}^{2-}\ (aq) + \cancel{SO_4}^{2-}(aq) + \cancel{2Na}^{+}\ (aq) + \cancel{2Cl}^{-}(aq)$$

No precipitation reaction

This particular example is important because all of the reactants and the products are aqueous, meaning they cancel out of the net ionic equation. There is no solid precipitate formed; therefore, no precipitation reaction occurs.

✓ Example 16.3.9

Write the net ionic equation for the potentially double displacement reactions. Make sure to include the states of matter and balance the equations.

a. $Fe(NO_3)_3\ _{(aq)} + NaOH(aq) \rightarrow$
b. $Al_2(SO_4)_3\ _{(aq)} + BaCl_2\ _{(aq)} \rightarrow$
c. $HI(aq) + Zn(NO_3)_2\ _{(aq)} \rightarrow$
d. $CaCl_2\ _{(aq)} + Na_3PO_4\ _{(aq)} \rightarrow$
e. $Pb(NO_3)_2\ _{(aq)} + K_2SO_4\ _{(aq)} \rightarrow$

Solutions

a. Regardless of physical state, the products of this reaction are $Fe(OH)_3$ and $NaNO_3$. The solubility rules predict that $NaNO_3$ is soluble because all nitrates are soluble (rule 2). However, $Fe(OH)_3$ is insoluble, because hydroxides are insoluble (rule 6) and Fe is not one of the cations which results in an exception. After dissociation, the ionic equation is as follows:

$$Fe^{3+}(aq) + NO_3^-\ _{(aq)} + Na^+(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3\ _{(s)} + Na^+(aq) + NO_3^-\ _{(aq)}$$

Canceling out spectator ions leaves the net ionic equation:

$$Fe^{3+}(aq) + OH^-(aq) \rightarrow Fe(OH)\ _{3(s)}$$

b. From the double replacement reaction, the products are $AlCl_3$ and $BaSO_4$. $AlCl_3$ is soluble because it contains a chloride (rule 3); however, $BaSO_4$ is insoluble: it contains a sulfate, but the Ba^{2+} ion causes it to be insoluble because it is one of the cations that causes an exception to rule 4. The ionic equation is (after balancing):

$$2Al^{3+}(aq) + 6Cl^-(aq) + 3Ba^{2+}(aq) + 3SO_4^{2-}\ _{(aq)} \rightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3BaSO_4\ _{(s)}$$

Canceling out spectator ions leaves the following net ionic equation:

$$Ba^{2+}(aq) + SO_4^{2-}\ _{(aq)} \rightarrow BaSO_4\ _{(s)}$$

c. From the double replacement reaction, the products HNO_3 and ZnI_2 are formed. Looking at the solubility rules, HNO_3 is soluble because it contains nitrate (rule 2), and ZnI_2 is soluble because iodides are soluble (rule 3). This means that both the products are aqueous (i.e. dissociate in water), and thus no precipitation reaction occurs.

d. The products of this double replacement reaction are $Ca_3(PO_4)_2$ and $NaCl$. Rule 1 states that $NaCl$ is soluble, and according to solubility rule 6, $Ca_3(PO_4)_2$ is insoluble. The ionic equation is:

$$Ca^{2+}(aq) + Cl^-(aq) + Na^+(aq) + PO_4^{3-}\ _{(aq)} \rightarrow Ca_3(PO_4)_2\ _{(s)} + Na^+(aq) + Cl^-(aq)$$

After canceling out spectator ions, the net ionic equation is given below:

$$Ca^{2+}(aq) + PO_4^{3-}\ _{(aq)} \rightarrow Ca_3(PO_4)_2\ _{(s)}$$

e. The first product of this reaction, $PbSO_4$, is soluble according to rule 4 because it is a sulfate. The second product, KNO_3, is also soluble because it contains nitrate (rule 2). Therefore, no precipitation reaction occurs.

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Summary

In contrast to K_{sp}, the ion product (Q_{sp}) describes concentrations that are not necessarily equilibrium concentrations. Comparing Q and K_{sp} enables us to determine whether a precipitate will form when solutions of two soluble salts are mixed. Adding a common cation or common anion to a solution of a sparingly soluble salt shifts the solubility equilibrium in the direction predicted by Le Chatelier's principle. The solubility of the salt is almost always decreased by the presence of a common ion.

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16.4: The Effects of pH on Solubility

Learning Objectives

- To understand why the solubility of many compounds depends on pH.

The solubility of many compounds depends strongly on the pH of the solution. For example, the anion in many sparingly soluble salts is the conjugate base of a weak acid that may become protonated in solution. In addition, the solubility of simple binary compounds such as oxides and sulfides, both strong bases, is often dependent on pH. In this section, we discuss the relationship between the solubility of these classes of compounds and pH.

The Effect of Acid–Base Equilibria the Solubility of Salts

We begin our discussion by examining the effect of pH on the solubility of a representative salt, $\mathrm{M^+A^-}$, where $\mathrm{A^-}$ is the conjugate base of the weak acid HA. When the salt dissolves in water, the following reaction occurs:

$$\mathrm{MA(s) \rightleftharpoons M^+(aq) + A^-(aq)}$$

with

$$K_{sp} = \mathrm{[M^+][A^-]}$$

The anion can also react with water in a hydrolysis reaction:

$$\mathrm{A^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HA(aq)} \tag{16.4.1}$$

Because of the reaction described in Equation 16.4.1, the predicted solubility of a sparingly soluble salt that has a basic anion such as S^{2-}, PO_4^{3-}, or CO_3^{2-} is increased. If instead a strong acid is added to the solution, the added H^+ will react essentially completely with A^- to form HA. This reaction decreases $[A^-]$, which decreases the magnitude of the ion product

$$Q = \mathrm{[M^+][A^-]} \tag{16.4.2}$$

According to Le Chatelier's principle, more MA will dissolve until $Q = K_{sp}$. Hence an acidic pH dramatically increases the solubility of virtually all sparingly soluble salts whose anion is the conjugate base of a weak acid. In contrast, pH has little to no effect on the solubility of salts whose anion is the conjugate base of a stronger weak acid or a strong acid, respectively (e.g., chlorides, bromides, iodides, and sulfates). For example, the hydroxide salt $Mg(OH)_2$ is relatively insoluble in water:

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \tag{16.4.3}$$

with

$$K_{sp} = 5.61 \times 10^{-12} \tag{16.4.4}$$

When acid is added to a saturated solution that contains excess solid $Mg(OH)_2$, the following reaction occurs, removing OH^- from solution:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \tag{16.4.5}$$

The overall equation for the reaction of $Mg(OH)_2$ with acid is thus

$$Mg(OH)_{2(s)} + 2H^+(aq) \rightleftharpoons Mg^{2+}(aq) + 2H_2O(l) \tag{16.4.6}$$

As more acid is added to a suspension of $Mg(OH)_2$, the equilibrium shown in Equation 16.4.6 is driven to the right, so more $Mg(OH)_2$ dissolves.

Such pH-dependent solubility is not restricted to salts that contain anions derived from water. For example, CaF_2 is a sparingly soluble salt:

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq) \tag{16.4.7}$$

with

$$K_{sp} = 3.45 \times 10^{-11} \tag{16.4.8}$$

When strong acid is added to a saturated solution of CaF_2, the following reaction occurs:

$$H^+(aq) + F^-(aq) \rightleftharpoons HF(aq) \tag{16.4.9}$$

Because the forward reaction decreases the fluoride ion concentration, more CaF_2 dissolves to relieve the stress on the system. The net reaction of CaF_2 with strong acid is thus

$$CaF_{2(s)} + 2H^+(aq) \rightarrow Ca^{2+}(aq) + 2HF(aq) \tag{16.4.10}$$

Example 16.4.1 shows how to calculate the solubility effect of adding a strong acid to a solution of a sparingly soluble salt.

> *Sparingly soluble salts derived from weak acids tend to be more soluble in an acidic solution.*

✓ Example 16.4.1

Lead oxalate (PbC_2O_4), lead iodide (PbI_2), and lead sulfate ($PbSO_4$) are all rather insoluble, with K_{sp} values of 4.8 × 10^{-10}, 9.8 × 10^{-9}, and 2.53 × 10^{-8}, respectively. What effect does adding a strong acid, such as perchloric acid, have on their relative solubilities?

Given: K_{sp} values for three compounds

Asked for: relative solubilities in acid solution

Strategy:

Write the balanced chemical equation for the dissolution of each salt. Because the strongest conjugate base will be most affected by the addition of strong acid, determine the relative solubilities from the relative basicity of the anions.

Solution

The solubility Equilibria for the three salts are as follows:

$$PbC_2O_{4(s)} \rightleftharpoons Pb^{2+}(aq) + C_2O^{2-}_{4(aq)}$$

$$PbI_{2(s)} \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

$$PbSO_{4(s)} \rightleftharpoons Pb^{2+}(aq) + SO^{2-}_{4(aq)}$$

The addition of a strong acid will have the greatest effect on the solubility of a salt that contains the conjugate base of a weak acid as the anion. Because HI is a strong acid, we predict that adding a strong acid to a saturated solution of PbI_2 will not greatly affect its solubility; the acid will simply dissociate to form H^+(aq) and the corresponding anion. In contrast, oxalate is the fully deprotonated form of oxalic acid (HO_2CCO_2H), which is a weak diprotic acid (pK_{a1} = 1.23 and pK_{a2} = 4.19). Consequently, the oxalate ion has a significant affinity for one proton and a lower affinity for a second proton. Adding a strong acid to a saturated solution of lead oxalate will result in the following reactions:

$$C_2O^{2-}_{4(aq)} + H^+(aq) \rightarrow HO_2CCO^-_{2(aq)}$$

$$HO_2CCO^-_{2(aq)} + H^+(aq) \rightarrow HO_2CCO_2H(aq)$$

These reactions will decrease $[C_2O_4^{2-}]$, causing more lead oxalate to dissolve to relieve the stress on the system. The pK_a of HSO_4^- (1.99) is similar in magnitude to the pK_{a1} of oxalic acid, so adding a strong acid to a saturated solution of $PbSO_4$ will result in the following reaction:

$$SO^{2-}_{4(aq)} + H^+(aq) \rightleftharpoons HSO^-_{4(aq)}$$

Because HSO_4^- has a pKa of 1.99, this reaction will lie largely to the left as written. Consequently, we predict that the effect of added strong acid on the solubility of $PbSO_4$ will be significantly less than for PbC_2O_4.

? Exercise 16.4.1

Which of the following insoluble salts—AgCl, Ag_2CO_3, Ag_3PO_4, and/or AgBr—will be substantially more soluble in 1.0 M HNO_3 than in pure water?

Answer

Ag_2CO_3 and Ag_3PO_4

Solubility Products and pH: https://youtu.be/XJ0s5SATZgQ

Caves and their associated pinnacles and spires of stone provide one of the most impressive examples of pH-dependent solubility Equilbria(part (a) in Figure 16.4.1:). Perhaps the most familiar caves are formed from limestone, such as Carlsbad Caverns in New Mexico, Mammoth Cave in Kentucky, and Luray Caverns in Virginia. The primary reactions that are responsible for the formation of limestone caves are as follows:

$$\mathrm{CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)} \tag{16.4.11}$$

$$\mathrm{HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)} \tag{16.4.12}$$

$$\mathrm{Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)} \tag{16.4.13}$$

Limestone deposits that form caves consist primarily of $CaCO_3$ from the remains of living creatures such as clams and corals, which used it for making structures such as shells. When a saturated solution of $CaCO_3$ in CO_2-rich water rises toward Earth’s surface or is otherwise heated, CO_2 gas is released as the water warms. $CaCO_3$ then precipitates from the solution according to the following equation (part (b) in Figure 16.4.1:):

$$Ca^{2+}(aq) + 2HCO^-_{3(aq)} \rightleftharpoons CaCO_{3(s)} + CO_{2(g)} + H_2O(l) \tag{16.4.14}$$

The forward direction is the same reaction that produces the solid called scale in teapots, coffee makers, water heaters, boilers, and other places where hard water is repeatedly heated.

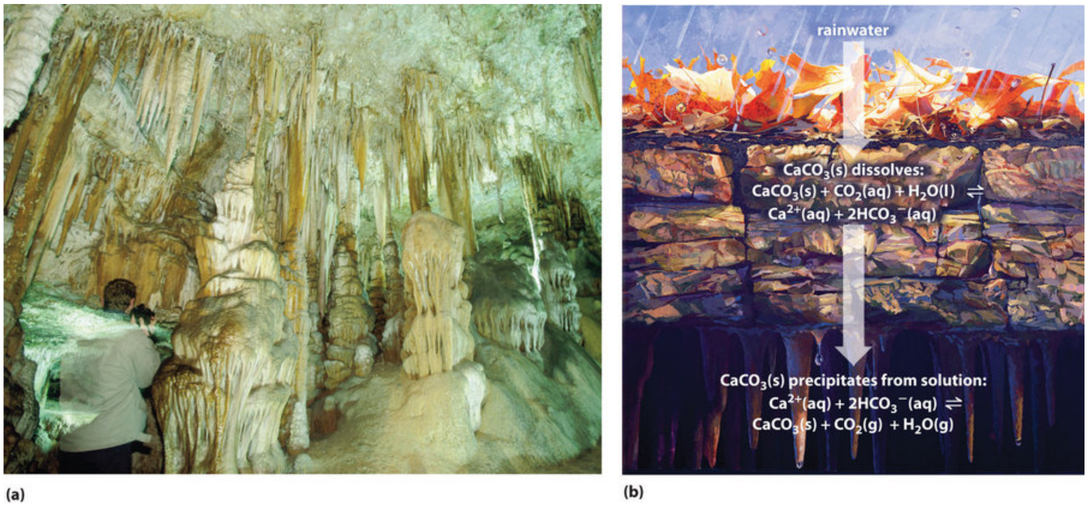


Figure 16.4.1: The Chemistry of Cave Formation. (a) This cave in Campanet, Mallorca, Spain, and its associated formations are examples of pH-dependent solubility equilibriums. (b) A cave forms when groundwater containing atmospheric CO_2, forming an acidic solution, dissolves limestone ($CaCO_3$) in a process that may take tens of thousands of years. As groundwater seeps into a cave, water evaporates from the solution of $CaCO_3$ in CO_2-rich water, producing a supersaturated solution and a shift in equilibrium that causes precipitation of the $CaCO_3$. The deposited limestone eventually forms stalactites and stalagmites.

When groundwater-containing atmospheric CO_2 (Equations 16.4.11 and 16.4.12) finds its way into microscopic cracks in the limestone deposits, $CaCO_3$ dissolves in the acidic solution in the reverse direction of Equation 16.4.14. The cracks gradually enlarge from 10–50 µm to 5–10 mm, a process that can take as long as 10,000 yr. Eventually, after about another 10,000 yr, a cave forms. Groundwater from the surface seeps into the cave and clings to the ceiling, where the water evaporates and causes the equilibrium in Equation 16.4.14 to shift to the right. A circular layer of solid $CaCO_3$ is deposited, which eventually produces a long, hollow spire of limestone called a stalactite that grows down from the ceiling. Below, where the droplets land when they fall from the ceiling, a similar process causes another spire, called a stalagmite, to grow up. The same processes that carve out hollows below ground are also at work above ground, in some cases producing fantastically convoluted landscapes like that of Yunnan Province in China (Figure 16.4.2).

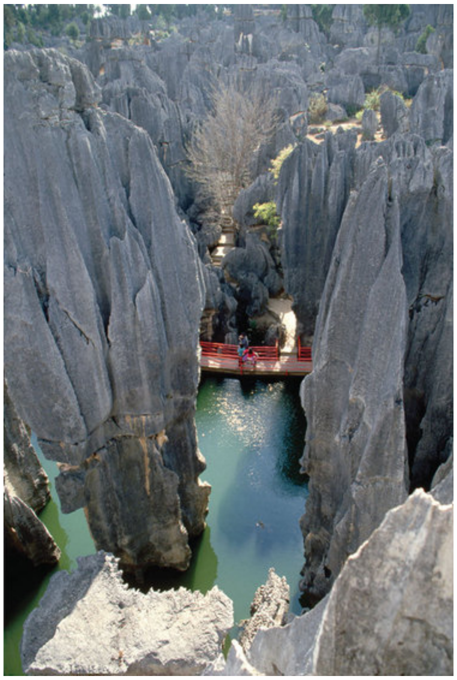


Figure 16.4.2: Solubility Equilbriain the Formation of Karst Landscapes. Landscapes such as the steep limestone pinnacles of the Stone Forest in Yunnan Province, China, are formed from the same process that produces caves and their associated formations.

Acidic, Basic, and Amphoteric Oxides and Hydroxides

One of the earliest classifications of substances was based on their solubility in acidic versus basic solution, which led to the classification of oxides and hydroxides as being either basic or acidic. **Basic oxides** and hydroxides either react with water to produce a basic solution or dissolve readily in aqueous acid. **Acidic oxides** or hydroxides either react with water to produce an acidic solution or are soluble in aqueous base. There is a clear correlation between the acidic or the basic character of an oxide and the position of the element combined with oxygen in the periodic table. Oxides of metallic elements are generally basic oxides, and oxides of nonmetallic elements are acidic oxides. Compare, for example, the reactions of a typical metal oxide, cesium oxide, and a typical nonmetal oxide, sulfur trioxide, with water:

$$Cs_2O(s) + H_2O(l) \rightarrow 2Cs^+(aq) + 2OH^-(aq) \tag{16.4.15}$$

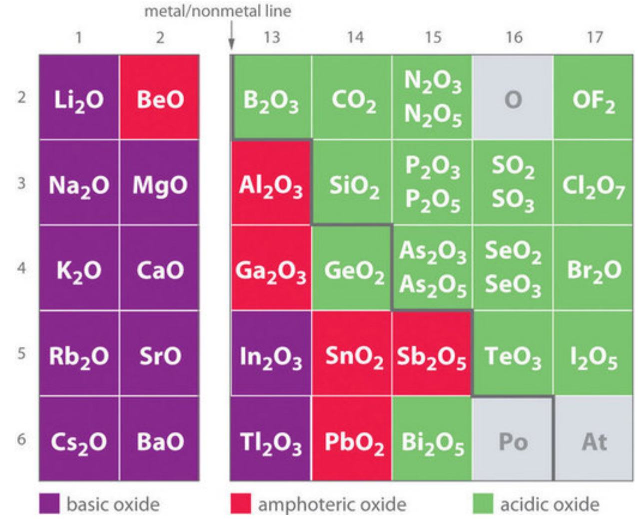
$$SO_{3(g)} + H_2O(l) \rightarrow H_2SO_{4(aq)} \tag{16.4.16}$$

Cesium oxide reacts with water to produce a basic solution of cesium hydroxide, whereas sulfur trioxide reacts with water to produce a solution of sulfuric acid—very different behaviors indeed

> *Metal oxides generally react with water to produce basic solutions, whereas nonmetal oxides produce acidic solutions.*

The difference in reactivity is due to the difference in bonding in the two kinds of oxides. Because of the low electronegativity of the metals at the far left in the periodic table, their oxides are best viewed as containing discrete Mn^+ cations and O^{2-} anions. At the other end of the spectrum are nonmetal oxides; due to their higher electronegativities, nonmetals form oxides with covalent bonds to oxygen. Because of the high electronegativity of oxygen, however, the covalent bond between oxygen and the other atom, E, is usually polarized: $E^{\delta+}$–$O^{\delta-}$. The atom E in these oxides acts as a Lewis acid that reacts with the oxygen atom of water to produce an oxoacid. Oxides of metals in high oxidation states also tend to be acidic oxides for the same reason: they contain covalent bonds to oxygen. An example of an acidic metal oxide is MoO_3, which is insoluble in both water and acid but dissolves in strong base to give solutions of the molybdate ion ($MoO_4{}^{2-}$):

$$MoO_{3(s)} + 2OH^-(aq) \rightarrow MoO^{2-}_{4(aq)} + H_2O(l) \tag{16.4.17}$$



	1	2	13	14	15	16	17
2	🟪 Li_2O	🟥 BeO	🟩 B_2O_3	🟩 CO_2	🟩 N_2O_3 N_2O_5	O	🟩 OF_2
3	🟪 Na_2O	🟪 MgO	🟥 Al_2O_3	🟩 SiO_2	🟩 P_2O_3 P_2O_5	🟩 SO_2 SO_3	🟩 Cl_2O_7
4	🟪 K_2O	🟪 CaO	🟥 Ga_2O_3	🟩 GeO_2	🟩 As_2O_3 As_2O_5	🟩 SeO_2 SeO_3	🟩 Br_2O
5	🟪 Rb_2O	🟪 SrO	🟪 In_2O_3	🟥 SnO_2	🟥 Sb_2O_5	🟩 TeO_3	🟩 I_2O_5
6	🟪 Cs_2O	🟪 BaO	🟪 Tl_2O_3	🟥 PbO_2	🟩 Bi_2O_5	Po	At

🟪 basic oxide 🟥 amphoteric oxide 🟩 acidic oxide

Figure 16.4.3: Classification of the Oxides of the Main Group Elements According to Their Acidic or Basic Character. There is a gradual transition from basic oxides to acidic oxides from the lower left to the upper right in the periodic table. Oxides of metallic elements are generally basic oxides, which either react with water to form a basic solution or dissolve in aqueous acid. In contrast, oxides of nonmetallic elements are acidic oxides, which either react with water to form an acidic solution or are soluble in aqueous base. Oxides of intermediate character, called amphoteric oxides, are located along a diagonal line between the two extremes. Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex ion. (Radioactive elements are not classified.)

As shown in Figure 16.4.3, there is a gradual transition from basic metal oxides to acidic nonmetal oxides as we go from the lower left to the upper right in the periodic table, with a broad diagonal band of oxides of intermediate character separating the two extremes. Many of the oxides of the elements in this diagonal region of the periodic table are soluble in both acidic and basic solutions; consequently, they are called **amphoteric oxides** (from the Greek ampho, meaning "both," as in amphiprotic).

Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex. As shown in Video 16.4.1, for example, mixing the amphoteric oxide $Cr(OH)_3$ (also written as $Cr_2O_3•3H_2O$) with water gives a muddy, purple-brown suspension. Adding acid causes the $Cr(OH)_3$ to dissolve to give a bright violet solution of $Cr^{3+}(aq)$, which contains the $[Cr(H_2O)_6]^{3+}$ ion, whereas adding strong base gives a green solution of the $[Cr(OH)_4]^{-}$ ion. The chemical equations for the reactions are as follows:

$$\mathrm{Cr(OH)_3(s) + 3H^+(aq) \rightarrow \underset{violet}{Cr^{3+}(aq)} + 3H_2O(l)} \tag{16.4.18}$$

$$\mathrm{Cr(OH)_3(s) + OH^-(aq) \rightarrow \underset{green}{[Cr(OH)_4]^-(aq)}} \tag{16.4.19}$$

Video* 16.4.1*: *Chromium(III) Hydroxide [$Cr(OH)_3$ or $Cr_2O_3•3H_2O$] is an Example of an Amphoteric Oxide. All three beakers originally contained a suspension of brownish purple $Cr(OH)_3(s)$ (center). When concentrated acid (6 M H_2SO_4) was added to the beaker on the left, $Cr(OH)_3$ dissolved to produce violet $[Cr(H_2O)_6]^{3+}$ ions and water. The addition of concentrated base (6 M NaOH) to the beaker on the right caused $Cr(OH)_3$ to dissolve, producing green $[Cr(OH)_4]^{-}$ ions. For a more complete description, see https://www.youtube.com/watch?v=IQNcLH6OZK0*

✓ Example 16.4.2

Aluminum hydroxide, written as either $Al(OH)_3$ or $Al_2O_3•3H_2O$, is amphoteric. Write chemical equations to describe the dissolution of aluminum hydroxide in (a) acid and (b) base.

Given: amphoteric compound

Asked for: dissolution reactions in acid and base

Strategy:

Using Equations 16.4.18and 16.4.19as a guide, write the dissolution reactions in acid and base solutions.

Solution

a. An acid donates protons to hydroxide to give water and the hydrated metal ion, so aluminum hydroxide, which contains three OH^{-} ions per Al, needs three H^{+} ions:

$$Al(OH)_{3(s)} + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$$

In aqueous solution, Al^{3+} forms the complex ion $[Al(H_2O)_6]^{3+}$.

b. In basic solution, OH^{-} is added to the compound to produce a soluble and stable poly(hydroxo) complex:

$$Al(OH)_{3(s)} + OH^-(aq) \rightarrow [Al(OH)_4]^-(aq)$$

Exercise 16.4.2

Copper(II) hydroxide, written as either Cu(OH)$_2$ or CuO•H$_2$O, is *amphoteric*. Write chemical equations that describe the dissolution of cupric hydroxide both in an acid and in a base.

Answer

$$Cu(OH)_{2(s)} + 2H^+(aq) \rightarrow Cu^{2+}(aq) + 2H_2O(l)$$

$$Cu(OH)_{2(s)} + 2OH^-(aq) \rightarrow [Cu(OH)_4]^{2}_{-(aq)}$$

Selective Precipitation Using pH

Many dissolved metal ions can be separated by the selective precipitation of the cations from solution under specific conditions. In this technique, pH is often used to control the concentration of the anion in solution, which controls which cations precipitate.

> *The concentration of anions in solution can often be controlled by adjusting the pH, thereby allowing the selective precipitation of cations.*

Suppose, for example, we have a solution that contains 1.0 mM Zn^{2+} and 1.0 mM Cd^{2+} and want to separate the two metals by selective precipitation as the insoluble sulfide salts, ZnS and CdS. The relevant solubility equilbria can be written as follows:

$$ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq) \tag{16.4.20}$$

with

$$K_{sp} = 1.6 \times 10^{-24} \tag{16.4.21}$$

and

$$CdS(s) \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq) \tag{16.4.22}$$

with

$$K_{sp} = 8.0 \times 10^{-27} \tag{16.4.23}$$

Because the S^{2-} ion is quite basic and reacts extensively with water to give HS$^-$ and OH$^-$, the solubility equilbria are more accurately written as $MS(s) \rightleftharpoons M^{2+}(aq) + HS^-(aq) + OH^-$ rather than $MS(s) \rightleftharpoons M^{2+}(aq) + S^{2-}(aq)$. Here we use the simpler form involving S^{2-}, which is justified because we take the reaction of S^{2-} with water into account later in the solution, arriving at the same answer using either equilibrium equation.

The sulfide concentrations needed to cause ZnS and CdS to precipitate are as follows:

$$K_{sp} = [Zn^{2+}][S^{2-}] \tag{16.4.24}$$

$$1.6 \times 10^{-24} = (0.0010\ M)[S^{2-}] \tag{16.4.25}$$

$$1.6 \times 10^{-21}\ M = [S^{2-}] \tag{16.4.26}$$

and

$$K_{sp} = [Cd^{2+}][S^{2-}] \tag{16.4.27}$$

$$8.0 \times 10^{-27} = (0.0010\ M)[S^{2-}] \tag{16.4.28}$$

$$8.0 \times 10^{-24}\ M = [S^{2-}] \tag{16.4.29}$$

Thus sulfide concentrations between 1.6 × 10^{-21} M and 8.0 × 10^{-24} M will precipitate CdS from solution but not ZnS. How do we obtain such low concentrations of sulfide? A saturated aqueous solution of H$_2$S contains 0.10 M H$_2$S at 20°C. The p$K_{a1}$for H$_2$S is 6.97, and pK_{a2} corresponding to the formation of [S^{2-}] is 12.90. The equations for these reactions are as follows:

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq) \tag{16.4.30}$$

with

$$pK_{a1} = 6.97 \text{ and hence } K_{a1} = 1.1 \times 10^{-7} \tag{16.4.31}$$

$$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq) \tag{16.4.32}$$

with

$$pK_{a2} = 12.90 \text{ and hence } K_{a2} = 1.3 \times 10^{-13} \tag{16.4.33}$$

We can show that the concentration of S^{2-} is 1.3 × 10^{-13} by comparing K_{a1} and K_{a2} and recognizing that the contribution to $[H^+]$ from the dissociation of HS^- is negligible compared with $[H^+]$ from the dissociation of H_2S. Thus substituting 0.10 M in the equation for K_{a1} for the concentration of H_2S, which is essentially constant regardless of the pH, gives the following:

$$K_{a1} = 1.1 \times 10^{-7} = \frac{[H^+][HS^-]}{[H_2S]} = \frac{x^2}{0.10 \text{ M}} \tag{16.4.34}$$

$$x = 1.1 \times 10^{-4} \text{ M} = [H^+] = [HS^-]$$

Substituting this value for $[H^+]$ and $[HS^-]$ into the equation for K_{a2},

$$K_{a2} = 1.3 \times 10^{-13} = \frac{[H^+][S^{2-}]}{[HS^-]} = \frac{(1.1 \times 10^{-4} \text{ M})x}{1.1 \times 10^{-4} \text{ M}} = x = [S^{2-}] \tag{16.4.35}$$

Although $[S^{2-}]$ in an H_2S solution is very low (1.3 × 10^{-13} M), bubbling H_2S through the solution until it is saturated would precipitate both metal ions because the concentration of S^{2-} would then be much greater than 1.6 × 10^{-21} M. Thus we must adjust $[S^{2-}]$ to stay within the desired range. The most direct way to do this is to adjust $[H^+]$ by adding acid to the H_2S solution (recall Le Chatelier's principle), thereby driving the equilibrium in Equation 16.4.33 to the left. The overall equation for the dissociation of H_2S is as follows:

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq) \tag{16.4.36}$$

Now we can use the equilibrium constant K for the overall reaction, which is the product of K_{a1} and K_{a2}, and the concentration of H_2S in a saturated solution to calculate the H^+ concentration needed to produce $[S^{2-}]$ of 1.6 × 10^{-21} M:

$$K = K_{a1}K_{a2} = (1.1 \times 10^{-7})(1.3 \times 10^{-13}) = 1.4 \times 10^{-20} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} \tag{16.4.37}$$

$$[H^+]^2 = \frac{K[H_2S]}{[S^{2-}]} = \frac{(1.4 \times 10^{-20})(0.10 \text{ M})}{1.6 \times 10^{-21} \text{ M}} = 0.88 \tag{16.4.38}$$

$$[H^+] = 0.94 \tag{16.4.39}$$

Thus adding a strong acid such as HCl to make the solution 0.94 M in H^+ will prevent the more soluble ZnS from precipitating while ensuring that the less soluble CdS will precipitate when the solution is saturated with H_2S.

✓ Example 16.4.3

A solution contains 0.010 M Ca^{2+} and 0.010 M La^{3+}. What concentration of HCl is needed to precipitate $La_2(C_2O_4)_3•9H_2O$ but not $Ca(C_2O_4)•H_2O$ if the concentration of oxalic acid is 1.0 M? K_{sp} values are 2.32 × 10^{-9} for $Ca(C_2O_4)$ and 2.5 × 10^{-27} for $La_2(C_2O_4)_3$; pK_{a1} = 1.25 and pK_{a2} = 3.81 for oxalic acid.

Given: concentrations of cations, K_{sp} values, and concentration and pK_a values for oxalic acid

Asked for: concentration of HCl needed for selective precipitation of $La_2(C_2O_4)_3$

Strategy:

A. Write each solubility product expression and calculate the oxalate concentration needed for precipitation to occur. Determine the concentration range needed for selective precipitation of $La_2(C_2O_4)_3•9H_2O$.
B. Add the equations for the first and second dissociations of oxalic acid to get an overall equation for the dissociation of oxalic acid to oxalate. Substitute the $[ox^{2-}]$ needed to precipitate $La_2(C_2O_4)_3•9H_2O$ into the overall equation for the dissociation of oxalic acid to calculate the required $[H^+]$.

Solution

A Because the salts have different stoichiometries, we cannot directly compare the magnitudes of the solubility products. Instead, we must use the equilibrium constant expression for each solubility product to calculate the concentration of oxalate needed for precipitation to occur. Using ox^{2-} for oxalate, we write the solubility product expression for calcium oxalate as follows:

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (0.010)[ox^{2-}] = 2.32 \times 10^{-9}$$

$$[ox^{2-}] = 2.32 \times 10^{-7}\ M$$

The expression for lanthanum oxalate is as follows:

$$K_{sp} = [La^{3+}]^2[ox^{2-}]^3 = (0.010)^2[ox^{2-}]^3 = 2.5 \times 10^{-27}$$

$$[ox^{2-}] = 2.9 \times 10^{-8}\ M$$

Thus lanthanum oxalate is less soluble and will selectively precipitate when the oxalate concentration is between $2.9 \times 10^{-8} M$ and $2.32 \times 10^{-7} M$.

B To prevent Ca^{2+} from precipitating as calcium oxalate, we must add enough H^+ to give a maximum oxalate concentration of 2.32×10^{-7} M. We can calculate the required $[H^+]$ by using the overall equation for the dissociation of oxalic acid to oxalate:

$$HO_2CCO_2H(aq) \rightleftharpoons 2H^+(aq) + C_2O^{2-}_{4(aq)} \tag{16.4.40}$$

$$K = K_{a1}K_{a2} = (10^{-1.25})(10^{-3.81}) = 10^{-5.06} = 8.7\times10^{-6}$$

Substituting the desired oxalate concentration into the equilibrium constant expression,

$$8.7 \times 10^{-6} = \frac{[\mathrm{H^+}]^2[\mathrm{ox}^{2-}]}{[\mathrm{HO_2CCO_2H}]} = \frac{[\mathrm{H^+}]^2(2.32 \times 10^{-7})}{1.0} \tag{16.4.41}$$

$$[\mathrm{H^+}] = 6.1\ \mathrm{M} \tag{16.4.42}$$

Thus adding enough HCl to give $[H^+]$ = 6.1 M will cause only $La_2(C_2O_4)_3•9H_2O$ to precipitate from the solution.

? Exercise 16.4.3

A solution contains 0.015 M Fe^{2+} and 0.015 M Pb^{2+}. What concentration of acid is needed to ensure that Pb^{2+} precipitates as PbS in a saturated solution of H_2S, but Fe^{2+} does not precipitate as FeS? K_{sp} values are 6.3×10^{-18} for FeS and 8.0×10^{-28} for PbS.

Answer

0.018 M H^+

Summary

The anion in sparingly soluble salts is often the conjugate base of a weak acid that may become protonated in solution, so the solubility of simple oxides and sulfides, both strong bases, often depends on pH. The anion in many sparingly soluble salts is the conjugate base of a weak acid. At low pH, protonation of the anion can dramatically increase the solubility of the salt. Oxides can be classified as acidic oxides or basic oxides. Acidic oxides either react with water to give an acidic solution or dissolve in strong base; most acidic oxides are nonmetal oxides or oxides of metals in high oxidation states. Basic oxides either react with water to give a basic solution or dissolve in strong acid; most basic oxides are oxides of metallic elements. Oxides or hydroxides that are soluble in both acidic and basic solutions are called amphoteric oxides. Most elements whose oxides exhibit amphoteric behavior are located along the diagonal line separating metals and nonmetals in the periodic table. In solutions that contain mixtures of dissolved metal ions, the pH can be used to control the anion concentration needed to selectively precipitate the desired cation.

Contributors and Attributions

- Anonymous

16.5: Complex Ions and Solubility

Learning Objectives

- To be introduced to complex ions, including ligands.

Previously, you learned that metal ions in aqueous solution are hydrated—that is, surrounded by a shell of usually four or six water molecules. A hydrated ion is one kind of a **complex ion** (or, simply, complex), a species formed between a central metal ion and one or more surrounding **ligands**, molecules or ions that contain at least one lone pair of electrons, such as the $[Al(H_2O)_6]^{3+}$ ion.

A complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base. Small, highly charged metal ions, such as Cu^{2+} or Ru^{3+}, have the greatest tendency to act as Lewis acids, and consequently, they have the greatest tendency to form complex ions.

As an example of the formation of complex ions, consider the addition of ammonia to an aqueous solution of the hydrated Cu^{2+} ion $\{[Cu(H_2O)_6]^{2+}\}$. Because it is a stronger base than H_2O, ammonia replaces the water molecules in the hydrated ion to form the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion. Formation of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex is accompanied by a dramatic color change, as shown in Figure 16.5.1. The solution changes from the light blue of $[Cu(H_2O)_6]^{2+}$ to the blue-violet characteristic of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion.

Figure 16.5.1: The Formation of Complex Ions. An aqueous solution of $CuSO_4$ consists of hydrated Cu^{2+} ions in the form of pale blue $[Cu(H_2O)_6]^{2+}$ (left). The addition of aqueous ammonia to the solution results in the formation of the intensely blue-violet $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions, usually written as $[Cu(NH_3)_4]^{2+}$ ion (right) because ammonia, a stronger base than H_2O, replaces water molecules from the hydrated Cu^{2+} ion. For a more complete description, see www.youtube.com/watch?v=IQNcLH6OZK0.

The Formation Constant

The replacement of water molecules from $[Cu(H_2O)_6]^{2+}$ by ammonia occurs in sequential steps. Omitting the water molecules bound to Cu^{2+} for simplicity, we can write the equilibrium reactions as follows:

$$\mathrm{Cu^{2+}(aq)} + \mathrm{NH_{3(aq)}} \rightleftharpoons \mathrm{[Cu(NH_3)]^{2+}_{(aq)}} \quad K_1 \tag{16.5.1}$$

$$\mathrm{[Cu(NH_3)]^{2+}_{(aq)}} + \mathrm{NH_{3(aq)}} \rightleftharpoons \mathrm{[Cu(NH_3)_2]^{2+}_{(aq)}} \quad K_2 \tag{16.5.2}$$

$$\mathrm{[Cu(NH_3)_2]^{2+}_{(aq)}} + \mathrm{NH_{3(aq)}} \rightleftharpoons \mathrm{[Cu(NH_3)_3]^{2+}_{(aq)}} \quad K_3 \tag{16.5.3}$$

$$\mathrm{[Cu(NH_3)_3]^{2+}_{(aq)}} + \mathrm{NH_{3(aq)}} \rightleftharpoons \mathrm{[Cu(NH_3)_4]^{2+}_{(aq)}} \quad K_4 \tag{16.5.4}$$

The sum of the stepwise reactions is the overall equation for the formation of the complex ion: The hydrated Cu^{2+} ion contains six H_2O ligands, but the complex ion that is produced contains only four NH_3 ligands, not six.

$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \tag{16.5.5}$$

The equilibrium constant for the formation of the complex ion from the hydrated ion is called the **formation constant (K_f)**. The equilibrium constant expression for K_f has the same general form as any other equilibrium constant expression. In this case, the expression is as follows:

$$K_\mathrm{f} = \frac{[\mathrm{[Cu(NH_3)_4]^{2+}}]}{[\mathrm{Cu^{2+}}][\mathrm{NH_3}]^4} = 2.1 \times 10^{13} = K_1K_2K_3K_4 \tag{16.5.6}$$

> *The formation constant (K_f) has the same general form as any other equilibrium constant expression.*

Water, a pure liquid, does not appear explicitly in the equilibrium constant expression, and the hydrated Cu^{2+}(aq) ion is represented as Cu^{2+} for simplicity. As for any equilibrium, the larger the value of the equilibrium constant (in this case, K_f), the more stable the product. With $K_f = 2.1 \times 10^{13}$, the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is very stable. The formation constants for some common complex ions are listed in Table 16.5.1.

Table 16.5.1: Common Complex Ions

	Complex Ion	**Equilibrium Equation**	**K_f**
Ammonia Complexes	$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.1×10^7
	$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
	$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	5.5×10^8
Cyanide Complexes	$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	1.1×10^{18}
	$[Ni(CN)_4]^{2-}$	$Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-}$	2.2×10^{31}
	$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1×10^{42}
Hydroxide Complexes	$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	4.6×10^{17}
	$[Cr(OH)_4]^-$	$Cr^{3+} + 4OH^- \rightleftharpoons [Cr(OH)_4]^-$	8.0×10^{29}
Halide Complexes	$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.2×10^{15}
	$[CdI_4]^{2-}$	$Cd^{2+} + 4I \rightleftharpoons [CdI_4]^{2-}$	2.6×10^5
	$[AlF_6]^{3-}$	$Al^{3+} + 6F^- \rightleftharpoons [AlF_6]^{3-}$	6.9×10^{19}
Other Complexes	$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}

*Reported values are overall formation constants. Source: Data from Lange’s Handbook of Chemistry, 15th ed. (1999).

Example 16.5.1

If 12.5 g of $\mathrm{Cu(NO_3)_2 \bullet 6\,H_2O}$ is added to 500 mL of 1.00 M aqueous ammonia, what is the equilibrium concentration of Cu^{2+}(aq)?

Given: mass of Cu^{2+} salt and volume and concentration of ammonia solution

Asked for: equilibrium concentration of Cu^{2+}(aq)

Strategy:

A. Calculate the initial concentration of Cu^{2+} due to the addition of copper(II) nitrate hexahydrate. Use the stoichiometry of the reaction shown in Equation 16.5.5 to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations of all species in solution.

B. Substitute the final concentrations into the expression for the formation constant (Equation 16.5.6) to calculate the equilibrium concentration of Cu^{2+}(aq).

Solution

Adding an ionic compound that contains Cu^{2+} to an aqueous ammonia solution will result in the formation of $[Cu(NH_3)_4]^{2+}$(aq), as shown in Equation 16.5.5. We assume that the volume change caused by adding solid copper(II) nitrate to aqueous ammonia is negligible.

A The initial concentration of Cu^{2+} from the amount of added copper nitrate prior to any reaction is as follows:

$$12.5\ \cancel{g}\ \mathrm{Cu(NO_3)_2 \cdot 6H_2O} \left(\frac{1\ \mathrm{mol}}{295.65\ \cancel{g}}\right)\left(\frac{1}{500\ m\cancel{L}}\right)\left(\frac{1000\ m\cancel{L}}{1\ \mathrm{L}}\right) = 0.0846\ \mathrm{M} \tag{16.5.7}$$

Because the stoichiometry of the reaction is four NH_3 to one Cu^{2+}, the amount of NH_3 required to react completely with the Cu^{2+} is 4(0.0846) = 0.338 M. The concentration of ammonia after complete reaction is 1.00 M − 0.338 M = 0.66 M. These results are summarized in the first two lines of the following table. Because the equilibrium constant for the reaction is large (2.1×10^{13}), the equilibrium will lie far to the right. Thus we will assume that the formation of $[Cu(NH_3)_4]^{2+}$ in the first step is complete and allow some of it to dissociate into Cu^{2+} and NH_3 until equilibrium has been reached. If we define x as the amount of Cu^{2+} produced by the dissociation reaction, then the stoichiometry of the reaction tells us that the change in the concentration of $[Cu(NH_3)_4]^{2+}$ is $-x$, and the change in the concentration of ammonia is $+4x$, as indicated in the table. The final concentrations of all species (in the bottom row of the table) are the sums of the concentrations after complete reaction and the changes in concentrations.

$$\mathrm{Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}}$$

	$[Cu^{2+}]$	$[NH_3]$	$[[Cu(NH_3)_4]^{2+}]$
initial	0.0846	1.00	0
after complete reaction	0	0.66	0.0846
change	$+x$	$+4x$	$-x$
final	x	$0.66 + 4x$	$0.0846 - x$

B Substituting the final concentrations into the expression for the formation constant (Equation 16.5.6) and assuming that $x << 0.0846$, which allows us to remove x from the sum and difference,

$$\begin{aligned} K_f &= \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{0.0846 - x}{x(0.66 + 4x)^4} \approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13} \\ x &= 2.1 \times 10^{-14} \end{aligned}$$

The value of x indicates that our assumption was justified. The equilibrium concentration of Cu^{2+}(aq) in a 1.00 M ammonia solution is therefore 2.1×10^{-14} M.

Exercise 16.5.1

The ferrocyanide ion $\{[Fe(CN)_6]^{4-}\}$ is very stable, with a K_f of 1×10^{35}. Calculate the concentration of cyanide ion in equilibrium with a 0.65 M solution of $K_4[Fe(CN)_6]$.

Answer

2×10^{-6} M

The Effect of the Formation of Complex Ions on Solubility

What happens to the solubility of a sparingly soluble salt if a ligand that forms a stable complex ion is added to the solution? One such example occurs in conventional black-and-white photography. Recall that black-and-white photographic film contains light-sensitive microcrystals of AgBr, or mixtures of AgBr and other silver halides. AgBr is a sparingly soluble salt, with a K_{sp} of 5.35×10^{-13} at 25°C. When the shutter of the camera opens, the light from the object being photographed strikes some of the crystals on the film and initiates a photochemical reaction that converts AgBr to black Ag metal. Well-formed, stable negative images appear in tones of gray, corresponding to the number of grains of AgBr converted, with the areas exposed to the most light being darkest. To fix the image and prevent more AgBr crystals from being converted to Ag metal during processing of the film, the unreacted AgBr on the film is removed using a complexation reaction to dissolve the sparingly soluble salt.

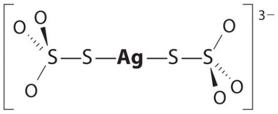
The reaction for the dissolution of silver bromide is as follows:

$$AgBr_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Br^{-}_{(aq)} \tag{16.5.8}$$

with

$$K_{sp} = 5.35 \times 10^{-13} \text{ at } 25^\circ\text{C} \tag{16.5.9}$$

The equilibrium lies far to the left, and the equilibrium concentrations of Ag^+ and Br^- ions are very low (7.31 × 10^{-7} M). As a result, removing unreacted AgBr from even a single roll of film using pure water would require tens of thousands of liters of water and a great deal of time. Le Chatelier's principle tells us, however, that we can drive the reaction to the right by removing one of the products, which will cause more AgBr to dissolve. Bromide ion is difficult to remove chemically, but silver ion forms a variety of stable two-coordinate complexes with neutral ligands, such as ammonia, or with anionic ligands, such as cyanide or thiosulfate ($S_2O_3^{2-}$). In photographic processing, excess AgBr is dissolved using a concentrated solution of sodium thiosulfate.



thiosulfate complex of Ag^+

The reaction of Ag^+ with thiosulfate is as follows:

$$Ag^+_{(aq)} + 2S_2O^{2-}_{3(aq)} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}_{(aq)} \tag{16.5.10}$$

with

$$K_f = 2.9 \times 10^{13} \tag{16.5.11}$$

The magnitude of the equilibrium constant indicates that almost all Ag^+ ions in solution will be immediately complexed by thiosulfate to form $[Ag(S_2O_3)_2]^{3-}$. We can see the effect of thiosulfate on the solubility of AgBr by writing the appropriate reactions and adding them together:

$$\mathrm{AgBr(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{Br^-(aq)} \quad K_{\mathrm{sp}} = 5.35 \times 10^{-13} \tag{16.5.12}$$

$$\mathrm{Ag^+(aq)} + 2\mathrm{S_2O_3^{2-}(aq)} \rightleftharpoons [\mathrm{Ag(S_2O_3)_2}]^{3-}\mathrm{(aq)} \quad K_{\mathrm{f}} = 2.9 \times 10^{13} \tag{16.5.13}$$

$$\mathrm{AgBr(s)} + 2\mathrm{S_2O_3^{2-}(aq)} \rightleftharpoons [\mathrm{Ag(S_2O_3)_2}]^{3-}\mathrm{(aq)} + \mathrm{Br^-(aq)} \quad K = K_{\mathrm{sp}}K_{\mathrm{f}} = 15 \tag{16.5.14}$$

Comparing K with K_{sp} shows that the formation of the complex ion increases the solubility of AgBr by approximately 3 × 10^{13}. The dramatic increase in solubility combined with the low cost and the low toxicity explains why sodium thiosulfate is almost universally used for developing black-and-white film. If desired, the silver can be recovered from the thiosulfate solution using any of several methods and recycled.

> *If a complex ion has a large K_f, the formation of a complex ion can dramatically increase the solubility of sparingly soluble salts.*

✓ Example 16.5.2

Due to the common ion effect, we might expect a salt such as AgCl to be much less soluble in a concentrated solution of KCl than in water. Such an assumption would be incorrect, however, because it ignores the fact that silver ion tends to form a two-coordinate complex with chloride ions ($AgCl_2^-$). Calculate the solubility of AgCl in each situation:

a. in pure water
b. in 1.0 M KCl solution, ignoring the formation of any complex ions
c. the same solution as in part (b) except taking the formation of complex ions into account, assuming that $AgCl_2^-$ is the only Ag^+ complex that forms in significant concentrations

At 25°C, $K_{sp} = 1.77 \times 10^{-10}$ for AgCl and $K_f = 1.1 \times 10^5$ for $AgCl_2^-$.

Given: K_{sp} of AgCl, K_f of $AgCl_2^-$, and KCl concentration

Asked for: solubility of AgCl in water and in KCl solution with and without the formation of complex ions

Strategy:

A. Write the solubility product expression for AgCl and calculate the concentration of Ag^+ and Cl^- in water.
B. Calculate the concentration of Ag^+ in the KCl solution.

C. Write balanced chemical equations for the dissolution of AgCl and for the formation of the $AgCl_2^-$ complex. Add the two equations and calculate the equilibrium constant for the overall equilibrium.
D. Write the equilibrium constant expression for the overall reaction. Solve for the concentration of the complex ion.

Solution

a. **A** If we let x equal the solubility of AgCl, then at equilibrium $[Ag+] = [Cl^-] = x$ M. Substituting this value into the solubility product expression,

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = x^2 = 1.77\times10^{-10}$$

$$x = 1.33\times10^{-5}$$

Thus the solubility of AgCl in pure water at 25°C is 1.33×10^{-5} M.

b. **B** If x equals the solubility of AgCl in the KCl solution, then at equilibrium $[Ag^+] = x$ M and $[Cl^-] = (1.0 + x)$ M. Substituting these values into the solubility product expression and assuming that $x << 1.0$,

$$K_{sp} = [Ag^+][Cl^-] = (x)(1.0 + x) \approx x(1.0) = 1.77\times10^{-10} = x$$

If the common ion effect were the only important factor, we would predict that AgCl is approximately five orders of magnitude less soluble in a 1.0 M KCl solution than in water.

c. **C** To account for the effects of the formation of complex ions, we must first write the equilibrium equations for both the dissolution and the formation of complex ions. Adding the equations corresponding to K_{sp} and K_f gives us an equation that describes the dissolution of AgCl in a KCl solution. The equilibrium constant for the reaction is therefore the product of K_{sp} and K_f:

$$\begin{aligned} AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} &= 1.77\times10^{-10} \qquad (16.5.15)\\ Ag^+(aq) + 2Cl^- \rightleftharpoons [AgCl_2]^- \quad K_f &= 1.1\times10^5 \qquad (16.5.16)\\ AgCl(s) + Cl^- \rightleftharpoons [AgCl_2]^- \quad K &= K_{sp}K_f = 1.9\times10^{-5} \qquad (16.5.17)\end{aligned}$$

D If we let x equal the solubility of AgCl in the KCl solution, then at equilibrium $[AgCl_2^-] = x$ and $[Cl^-] = 1.0 - x$. Substituting these quantities into the equilibrium constant expression for the net reaction and assuming that $x << 1.0$,

$$K = \frac{[AgCl_2^-]}{[Cl^-]} = \frac{x}{1.0-x} \approx 1.9\times10^{-5} = x$$

That is, AgCl dissolves in 1.0 M KCl to produce a 1.9×10^{-5} M solution of the $AgCl_2^-$ complex ion. Thus we predict that AgCl has approximately the same solubility in a 1.0 M KCl solution as it does in pure water, which is 10^5 times greater than that predicted based on the common ion effect. (In fact, the measured solubility of AgCl in 1.0 M KCl is almost a factor of 10 greater than that in pure water, largely due to the formation of other chloride-containing complexes.)

? Exercise 16.5.2

Calculate the solubility of mercury(II) iodide (HgI_2) in each situation:

a. pure water
b. a 3.0 M solution of NaI, assuming $[HgI_4]^{2-}$ is the only Hg-containing species present in significant amounts

$$K_{sp} = 2.9 \times 10^{-29} \text{ for } HgI_2 \text{ and } K_f = 6.8 \times 10^{29} \text{ for } [HgI_4]^{2-}.$$

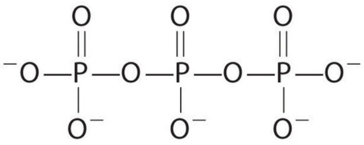
Answer a

1.9×10^{-10} M

Answer a

1.4 M

Complexing agents, molecules or ions that increase the solubility of metal salts by forming soluble metal complexes, are common components of laundry detergents. Long-chain carboxylic acids, the major components of soaps, form insoluble salts with Ca^{2+} and Mg^{2+}, which are present in high concentrations in “hard” water. The precipitation of these salts produces a bathtub ring and gives a gray tinge to clothing. Adding a complexing agent such as pyrophosphate ($O_3POPO_3^{4-}$, or $P_2O_7^{4-}$) or triphosphate ($P_3O_{10}^{5-}$) to detergents prevents the magnesium and calcium salts from precipitating because the equilibrium constant for complex-ion formation is large:



triphosphate

$$\mathrm{Ca^{2+}(aq)+O_3POPO_4^{4-}(aq)\rightleftharpoons[Ca(O_3POPO_3)]^{2-}(aq)} \tag{16.5.18}$$

with

$$K_f=4\times10^4 \tag{16.5.19}$$

However, phosphates can cause environmental damage by promoting eutrophication, the growth of excessive amounts of algae in a body of water, which can eventually lead to large decreases in levels of dissolved oxygen that kill fish and other aquatic organisms. Consequently, many states in the United States have banned the use of phosphate-containing detergents, and France has banned their use beginning in 2007. “Phosphate-free” detergents contain different kinds of complexing agents, such as derivatives of acetic acid or other carboxylic acids. The development of phosphate substitutes is an area of intense research.

Commercial water softeners also use a complexing agent to treat hard water by passing the water over ion-exchange resins, which are complex sodium salts. When water flows over the resin, sodium ion is dissolved, and insoluble salts precipitate onto the resin surface. Water treated in this way has a saltier taste due to the presence of Na^+, but it contains fewer dissolved minerals.

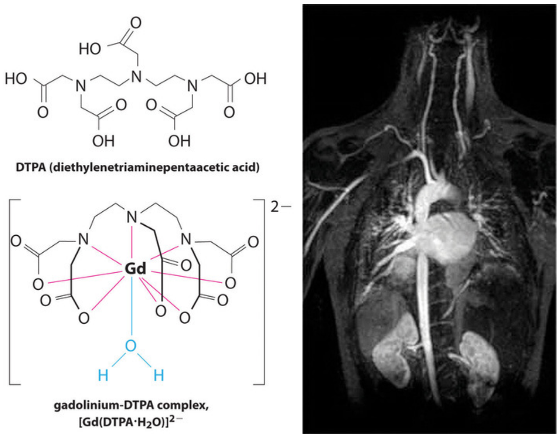


Figure 16.5.2: An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

Another application of complexing agents is found in medicine. Unlike x-rays, magnetic resonance imaging (MRI) can give relatively good images of soft tissues such as internal organs. MRI is based on the magnetic properties of the ^1H nucleus of hydrogen atoms in water, which is a major component of soft tissues. Because the properties of water do not depend very much on whether it is inside a cell or in the blood, it is hard to get detailed images of these tissues that have good contrast. To solve this problem, scientists have developed a class of metal complexes known as “MRI contrast agents.” Injecting an MRI contrast agent into a patient selectively affects the magnetic properties of water in cells of normal tissues, in tumors, or in blood vessels and allows doctors to “see” each of these separately (Figure 16.5.2). One of the most important metal ions for this application is Gd^{3+}, which with seven unpaired electrons is highly paramagnetic. Because $Gd^{3+}(aq)$ is quite toxic, it must be administered as a very stable complex that does not dissociate in the body and can be excreted intact by the kidneys. The complexing agents used for gadolinium are ligands such as $DTPA^{5-}$ (diethylene triamine pentaacetic acid), whose fully protonated form is shown here.

Summary

The formation of complex ions can substantially increase the solubility of sparingly soluble salts if the complex ion has a large K_f. A complex ion is a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons. Small, highly charged metal ions have the greatest tendency to act as Lewis acids and form complex ions. The equilibrium constant for the formation of the complex ion is the formation constant (K_f). The formation of a complex ion by adding a complexing agent increases the solubility of a compound.

16.6: A Deeper Look: Selective Precipitation of Ions

Learning Objectives

- To know how to separate metal ions by selective precipitation.
- To understand how several common metal cations can be identified in a solution using selective precipitation.

The composition of relatively complex mixtures of metal ions can be determined using **qualitative analysis**, a procedure for discovering the identity of metal ions present in the mixture (rather than quantitative information about their amounts). The procedure used to separate and identify more than 20 common metal cations from a single solution consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively less selective until almost all of the metal ions are precipitated, as illustrated in Figure 16.6.1.

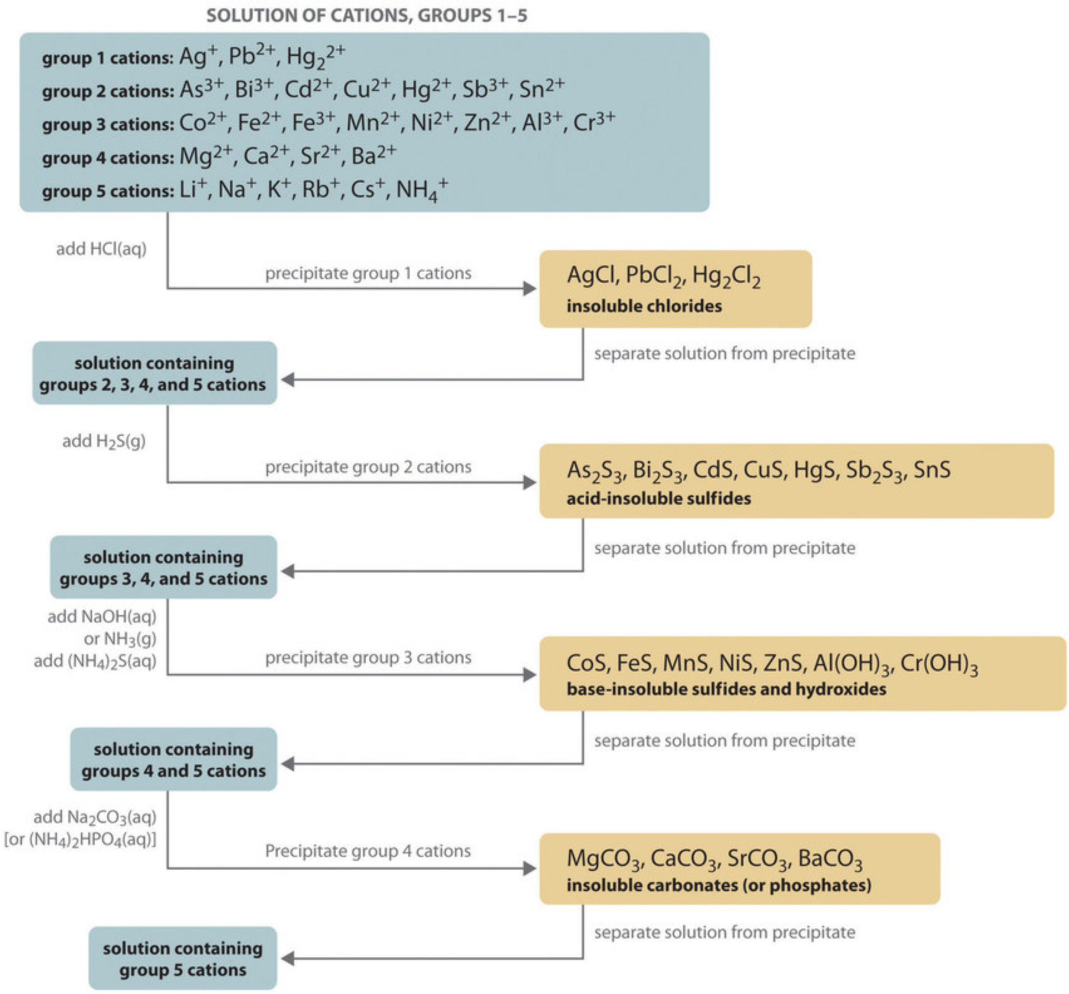


Figure 16.6.1: Steps in a Typical Qualitative Analysis Scheme for a Solution That Contains Several Metal Ions

Group 1: Insoluble Chlorides

Most metal chloride salts are soluble in water; only Ag^+, Pb^{2+}, and Hg_2^{2+} form chlorides that precipitate from water. Thus the first step in a qualitative analysis is to add about 6 M HCl, thereby causing $AgCl$, $PbCl_2$, and/or Hg_2Cl_2 to precipitate. If no precipitate forms, then these cations are not present in significant amounts. The precipitate can be collected by filtration or centrifugation.

Group 2: Acid-Insoluble Sulfides

Next, the acidic solution is saturated with H_2S gas. Only those metal ions that form very insoluble sulfides, such as As^{3+}, Bi^{3+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Sb^{3+}, and Sn^{2+}, precipitate as their sulfide salts under these acidic conditions. All others, such as Fe^{2+} and Zn^{2+}, remain in solution. Once again, the precipitates are collected by filtration or centrifugation.

Group 3: Base-Insoluble Sulfides (and Hydroxides)

Ammonia or $NaOH$ is now added to the solution until it is basic, and then $(NH_4)_2S$ is added. This treatment removes any remaining cations that form insoluble hydroxides or sulfides. The divalent metal ions Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} precipitate as their sulfides, and the trivalent metal ions Al^{3+} and Cr^{3+} precipitate as their hydroxides: $Al(OH)_3$ and $Cr(OH)_3$. If the mixture contains Fe^{3+}, sulfide reduces the cation to Fe^{2+}, which precipitates as FeS.

Group 4: Insoluble Carbonates or Phosphates

The next metal ions to be removed from solution are those that form insoluble carbonates and phosphates. When Na_2CO_3 is added to the basic solution that remains after the precipitated metal ions are removed, insoluble carbonates precipitate and are collected. Alternatively, adding $(NH_4)_2HPO_4$ causes the same metal ions to precipitate as insoluble phosphates.

Group 5: Alkali Metals

At this point, we have removed all the metal ions that form water-insoluble chlorides, sulfides, carbonates, or phosphates. The only common ions that might remain are any alkali metals (Li^+, Na^+, K^+, Rb^+, and Cs^+) and ammonium (NH_4^+). We now take a second sample from the original solution and add a small amount of $NaOH$ to neutralize the ammonium ion and produce NH_3. (We cannot use the same sample we used for the first four groups because we added ammonium to that sample in earlier steps.) Any ammonia produced can be detected by either its odor or a litmus paper test. A flame test on another original sample is used to detect sodium, which produces a characteristic bright yellow color. The other alkali metal ions also give characteristic colors in flame tests, which allows them to be identified if only one is present.

Metal ions that precipitate together are separated by various additional techniques, such as forming complex ions, changing the pH of the solution, or increasing the temperature to redissolve some of the solids. For example, the precipitated metal chlorides of group 1 cations, containing Ag^+, Pb^{2+}, and Hg_2^{2+}, are all quite insoluble in water. Because $PbCl_2$ is much more soluble in hot water than are the other two chloride salts, however, adding water to the precipitate and heating the resulting slurry will dissolve any $PbCl_2$ present. Isolating the solution and adding a small amount of Na_2CrO_4 solution to it will produce a bright yellow precipitate of $PbCrO_4$ if Pb^{2+} were in the original sample (Figure $16.6.2$).

Figure 16.6.2: When a small amount of Na_2CrO_4 solution is added to a sample containing Pb^{2+} ions in water, a bright yellow precipitate of $PbCrO_4$ forms. (CC BY-SA 3.0 Unported; PRHaney via Wikipedia).

As another example, treating the precipitates from group 1 cations with aqueous ammonia will dissolve any $AgCl$ because Ag^+ forms a stable complex with ammonia: $[Ag(NH_3)_2]^+$. In addition, Hg_2Cl_2 disproportionates in ammonia.

$$2\,Hg_2^{2+} \rightarrow Hg + Hg^{2+}$$

to form a black solid that is a mixture of finely divided metallic mercury and an insoluble mercury(II) compound, which is separated from solution:

$$Hg_2Cl_2(s) + 2\,NH_3(aq) \rightarrow Hg(l) + Hg(NH_2)Cl(s) + NH_4^+(aq) + Cl^-(aq)$$

Any silver ion in the solution is then detected by adding HCl, which reverses the reaction and gives a precipitate of white $AgCl$ that slowly darkens when exposed to light:

$$[\mathrm{Ag(NH_3)_2}]^+(\mathrm{aq}) + 2\,\mathrm{H}^+(\mathrm{aq}) + \mathrm{Cl}^-(\mathrm{aq}) \rightarrow \mathrm{AgCl(s)} + 2\,\mathrm{NH_4^+}(\mathrm{aq})$$

Similar but slightly more complex reactions are also used to separate and identify the individual components of the other groups.

Summary

In qualitative analysis, the identity, not the amount, of metal ions present in a mixture is determined. The technique consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively less selective until almost all the metal ions are precipitated. Other additional steps are needed to separate metal ions that precipitate together.

16.E: Solubility and Precipitation (Exercises)

These are homework exercises to accompany the Textmap created for "Principles of Modern Chemistry" by Oxtoby et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here.

Q5

State the balanced equation representing the dissolution of potassium chromate and write its solubility product expression.

Answer

$$\mathrm{K_2CrO_4 \rightleftharpoons 2K^+ + CrO_4^{2-}}$$

$$\mathrm{K_{sp} = [K^+]^2[CrO_4^{2-}]}$$

Q11

Consider Mercury(I) bromide. Estimate the concentration of Hg_2^{2+} and Br^- given the K_{sp} as 5.6 x 10^{-23}.

Answer

$$\mathrm{Hg_2Br_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\,Br^-(aq)} \tag{16.E.1}$$

$$K_{sp} = 5.6 \cdot 10^{-23} = [Hg_2^{2+}][Br^-]^2 = x(2x)^2 \tag{16.E.2}$$

$$\mathrm{x = 2.41 \times 10^{-8} = [Hg_2^{2+}]}$$

$$\mathrm{[Br^-] = 4.82 \times 10^{-8}}$$

Q13

The solubility product constant of Calcium chlorate ($Ca(ClO_3)_2$) of water is 7.1 × 10^{-7} at 25°C. How many grams of $Ca(ClO_3)_2$ were dissolved in 750 mL?

Answer

First, write out the solubility product constant expression for $\mathrm{Ca(ClO_3)_2}$

$$\mathrm{Ca(ClO_3)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,ClO_3^-(aq)}$$

$$\mathrm{K_{sp} = [Ca^{2+}][ClO_3^-]^2}$$

ICE Table	$Ca(ClO_3)_2$	Ca^{2+}	ClO_3^-
Initial	-	0	0
Change	-	+x	+2x
Equilibrium	-	x	2x

$Ca(ClO_3)_2$ does not matter because it is a solid

$$\mathrm{K_{sp} = [x] \cdot [2x]^2}$$

$$\mathrm{7.1 \times 10^{-7} = 4x^3}$$

$$\mathrm{x = 0.0056\ M}$$

The number of moles of Ca^{2-} is the same as the number of moles of $Ca(ClO_3)_2$ because matter cannot be created or destroyed.

$$\mathrm{\frac{0.0056\ moles}{L} \times 0.750\ L = 0.0042\ moles\ Ca(ClO_3)_2}$$

Finally, the mass can be calculated by multiplying the number of moles with the molar mass:

$$0.0042\ \text{molesCa}(\text{ClO}_3)_2 \times (\frac{206.98\ \text{g}}{1\ \text{mole}}) = 0.872\ \text{g}$$

Q15

At 25°C, water dissolves 0.8108g of $PbCl_2$ per liter, calculate the K_{sp} of $PbCl_2$ at 25°C.

Answer

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

$$K_{sp} = [Pb^{2+}] \cdot [Cl^-]^2$$

$$n(PbCl_2) = \frac{0.8108g}{278.1g/mol} = 2.9155 \times 10^{-3} mol = n(Pb^{2+}) = 0.5n(Cl^-)$$

$$K_{sp} = \frac{2.9155 \times 10^{-3} mol}{1L} \cdot (\frac{5.831 \times 10^{-3} mol}{1L})^2 = 9.91 \times 10^{-8}$$

Q17

0.986635g of $BaCO_3$ is dissolved in $1.00dm^3$ water at 80°C. the solution was then cooled down to 25°C. Given that the Ksp of $BaCO_3$ in water is $2.58x10^{-9}$ at 25°C, determine with an explanation whether or not a precipitate will form at 25°C.

Answer

x moles of $BaCO_3$ dissolves into x moles of Ba^{2+} and x moles CO_3^{2-} due to equal stoichiometric coefficients (since solution is 1.00L, the moles also equal to molarities). Calculate the moles of $BaCO_3$, then square the result to find Qsp, then compare Qsp to Ksp at 25°C.

$$\text{moles of BaCO}_3 = 0.986635\ \text{g} \times (137.327\frac{\text{g}}{\text{mol}} + 12\frac{\text{g}}{\text{mol}} + 3 \times 16\frac{\text{g}}{\text{mol}}) = 5.0 \times 10^{-3}\ \text{mol}$$

$$\text{Q}_{\text{sp}} = (5.0 \times 10^{-3}\ \text{M})^2 = 2.5 \times 10^{-5}$$

$$2.5 \times 10^{-5} > 2.58 \times 10^{-9}$$

$$\text{Q}_{\text{sp}} > \text{K}_{\text{sp}}$$

Therefore, precipitate forms.

Q19

Suppose that you take a solution of 500.0-mL of 0.001234 M FeF_2 and mix it well with a 500.0-mL solution of 0.003142 M KOH at 25°C. Given that $\text{K}_{\text{sp}} = 4.87 \times 10^{-17}$ is for $Fe(OH)_2$, determine whether or not a precipitate will be formed from the mixture.

Answer

Before starting any calculations it is important to write down the equation for precipitation of the $Fe(OH)_2$.

$$\text{Fe(OH)}_2(s) \rightleftharpoons \text{Fe}^{2+}(aq) + 2\ \text{OH}^-(aq)$$

State the solubility product expression and set it equal to the solubility product constant:

$$K_{sp} = [Fe^2+][OH-]^2 = 4.87 \times 10^{-17}$$

Now that the essential basic steps are out of the way, find the new concentrations of both Fe^{2+} Fe^{2+} and OH^- by first finding the number of moles in the original unmixed solutions and then dividing that number by the total new volume in liters.

$$\text{moles Fe}^{2+} = 500\ \cancel{mL} \left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.001234\ \text{mol}}{1\ \cancel{L}}\right) = 6.17 \times 10^{-4}\ \text{mol Fe}^{2+}$$

$$[Fe^{2+}] = \left(\frac{6.17\times10^{-4}\text{ mol Fe}^{2+}}{1000\ \cancel{\text{mL}}}\right)\left(\frac{1000\ \cancel{\text{mL}}}{1\text{ L}}\right) = 6.17\times10^{-4}\text{ M Fe}^{2+}$$

$$\text{moles OH-} = 500\ \cancel{\text{mL}}\left(\frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}}\right)\left(\frac{0.003142\text{ mol}}{1\ \cancel{\text{L}}}\right) = 1.57\times10^{-3}\text{ mol OH-}$$

$$[OH-] = \left(\frac{1.57\times10^{-3}\text{ mol OH-}}{1000\ \cancel{\text{mL}}}\right)\left(\frac{1000\ \cancel{\text{mL}}}{1\text{ L}}\right) = 1.57\times10^{-3}\text{ M OH-}$$

Now that the new concentrations have been found they can be substituted in the Q_{sp} equation and solved for.

$$Q_{sp} = [6.17\times10^{-4}][1.57\times10^{-3}]^2 = 1.52\times10^{-9}$$

As shown above the $Q_{sp} > K_{sp}$, therefore a precipitate does in fact form.

Q23

The solubility product constant of Ag_2CO_3 is 8.1×10^{-12} at 25°C. Calculate $[Ag^+]$ and $[CO_3^{2-}]$ in the solution at equilibrium when 6 mL of 0.1M Na_2CO_3 are mixed with 3 mL of 0.5M $AgNO_3$.

Answer

$$2AgNO_{3(aq)} + Na_2CO_{3(aq)} \rightleftharpoons Ag_2CO_{3(s)} + 2NaNO_{3(aq)} \tag{16.E.3}$$

$$mole_{AgNO_3} = mole_{Ag^+} = (0.003\ L)(0.5\ M) = 1.5\times10^{-3}\ mol \tag{16.E.4}$$

$$mole_{Na_2CO_3} = mole_{CO_3^{2-}} = (0.006\ L)(0.1\ M) = 6\times10^{-4}\ mol \tag{16.E.5}$$

$$Total\ Volume = 3\ mL + 6\ mL = 9\ mL = 0.009\ L \tag{16.E.6}$$

$$M_{CO_3^{2-}} = \frac{6\times10^{-4} mol}{0.009\ L} = 0.0667\ M \tag{16.E.7}$$

$$M_{Ag^+} = \frac{1.5\times10^{-3}\ mol}{0.009\ L} = 0.1667\ M \tag{16.E.8}$$

$$2Ag^+ + CO_3^{2-} \rightarrow Ag_2CO_{3(s)} \tag{16.E.9}$$

	$2\,Ag^+$	CO_3^{2-}	Ag_2CO_3
Initial	0.1667M	0.0667M	X
Change	-2x	-x	X
Equilibrium	0.1667-2x	0.0667-x	X

$$K_{sp} = 8.1\times10^{-12} = [CO_3^-][Ag^+]^2 \tag{16.E.10}$$

$$8.1\times10^{-12} = [0.0667 - x][0.1667 - 2x]^2 \tag{16.E.11}$$

$$x = 0.06669999M \tag{16.E.12}$$

$$[Ag^+] = 0.1667 - 2x = 0.03336M \tag{16.E.13}$$

$$[CO_3^{2-}] = 0.0667 - x = 7.30\times10^{-9} \tag{16.E.14}$$

Q25

Your nemesis has prepared a perfectly saturated solution of CaF_2. To sabotage their work, you add 10 M NaF to their solution. How many grams of CaF_2 fall out of solution if they had prepared 500 mL.

$CaF_2 : K_{sp} = 4.0\times10^{-11}$

Answer

First, calculate the molar solubility of CaF_2 from it's K_{sp} with the expression:

$$K_{sp} = (s)(2s)^2 = 4s^3$$

$$4.0 \times 10^{-11} = 4s^3$$

$$s = 2.15 \times 10^{-4}$$

Then, create an ICE table for the addition of F^- as NaF:

Products	F^-	Ca^{2+}
Initial	s+10	s
Change	-2x	-x
Equilibrium	(s+10) -2x	s-x

Now, it's reasonable to assume that 10>>x and s, so our expression simplifies to:

$$K_{sp} = 10^2(s - x)$$

Solving for x yields the moles/L which fall out, so multiplying x by 0.5 L (500 mL) yields the correct answer.

$$K_{sp} = 4.0 \times 10^{-11} = 10^2(s - x)$$

$$x = 0.000215\ M$$

$$0.5\ L(0.000215\ M)(78.07\ \frac{g}{mol}) = 0.00839\ g$$

Q27

Given copper(II) hydroxide, $Cu(OH)_2$. The concentration of Cu^{2+} and OH^- at equilibrium in 25°C water is 1.765 x 10^{-7}M and 3.530 x 10^{-7}M respectively.

a. Find the K_{sp}.
b. Find the molar solubility of $Cu(OH)_2$ in 0.100M NaOH.

Answer

$$Cu(OH)_{2(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \tag{16.E.15}$$

1)

Since the solubilities given are already at equilibrium, K_{sp} is found as such:

$$K_{sp} = [Cu^{2+}][OH^-]^2 = (1.765 \times 10^{-7} M)(3.530 \times 10^{-7} M)^2 = 2.2 \times 10^{-20} \tag{16.E.16}$$

2)

ICE Table	$Cu(OH)_{2(s)}$	$Cu^{2+}_{(aq)}$	$OH^-_{(aq)}$
Initial	-	0	0.100
Change	-	+Z	+2Z
Equilibrium	-	Z	0.100+2Z

Apply the ice table result to the K_{sp} found in 1), we get

$$K_{sp} = 2.2 \times 10^{-20} = [Cu^{2+}][OH^-]^2 = (z)(0.100 + 2z)^2 \tag{16.E.17}$$

Z can be found either by plugging in quadratic formula or finding intersection in a graphing calculator.

$$K_{sp} = 2.2 \times 10^{-20} = (z)(0.100 + 2z)^2 \tag{16.E.18}$$

$$\text{z} = 2.2 \times 10^{-18} \text{ M}$$

Q28

Barium Carbonate ($BaCO_3$) has a solubility product of K_{sp} = 8.1 x 10^{-9} at 25°C for the equilibrium

$$BaCO_3 \rightleftharpoons Ba^{2+} + CO_3^{2-}$$

a. Calculate the molar solubility of Barium Carbonate in the water at 25°C.
b. Calculate the molar solubility of Barium Carbonate in 0.1M $PbCO_3$.

Answer

a) The expression for solubility product is

$$[Ba^{2+}][{CO_3}^{2-}] = K_{sp} \tag{16.E.19}$$

Let

$$[Ba^{2+}] = S \tag{16.E.20}$$

$$S^2 = K_p = 8.1 \times 10^{-9} \tag{16.E.21}$$

Hence, S = 9 x 10^{-5}

Molar Solubility of Barium Carbonate = 9 x 10^{-5} M

b) due to the common ion effect, $PbCO_3$ reduces the molar solubility of Barium Carbonate.

$$BaCO_3 \rightleftharpoons Ba^{2+} \quad + \quad CO_3^{2-} \tag{16.E.22}$$

	Ba^{2+}	CO_3^{2-}
Initial	0	0.1
Change	+S	+S
Final	+S	0.1+S

$$[Ba^{2+}][{CO_3}^{2-}] = K_{sp} \tag{16.E.23}$$

$$S(0.1 + S) = K_{sp} \tag{16.E.24}$$

$$S + 0.1 \approx 0.1 \tag{16.E.25}$$

⇒

$$S(0.1) = K_{sp} \tag{16.E.26}$$

⇒

$$S = \frac{8.1 \times 10^{-9}}{0.1} = 8.1 \times 10^{-8} \tag{16.E.27}$$

⇒

$$S = 8.1 \times 10^{-8} << 0.1 \tag{16.E.28}$$

Hence, Molar Solubility = 8.1 x 10^{-8} M

Q33

Determine how will the solubility of the following compounds change (increase, decrease, or unchanged) if the neutral solution is made to be more acidic. Explain your answer in one sentence.

a. NO_3^-
b. NH_3
c. CO_3^{2-}

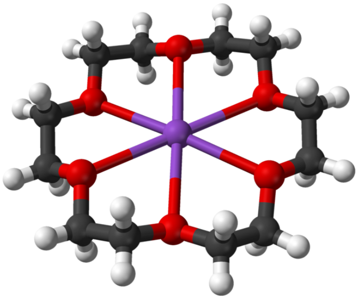
Answer

As the acidity of a solution increases, the solubility of salts consist of conjugate bases of weak acids will increases.

a. NO_3^- is the conjugate base of a strong acid so the solubility will not change
b. NH_3 is the conjugate base of a weak acid so the solubility will increase
c. CO_3^{2-} is also a conjugate base of a weak acid so the solubility will increase

Q37

18-crown-6, or $C_{12}H_{24}O_6$, is an organic compound that can bind to group 1 metal ions by wrapping around them when in aqueous solutions. Due to its particular size, it can fit the K^+ ion better than any other.



Ball-and-stick model of the 18-crown-6 potassium complex in crystalline (18-crown-6)potassium chlorochromate, [K($C_{12}H_{24}O_6$)][$CrClO_3$]. X-ray diffraction data from S. A. Kotlyar, R. I. Zubatyuk, O. V. Shishkin, G. N. Chuprin, A. V. Kiriyak and G. L. Kamalov (February 2005). "(18-Crown-6)potassium chlorochromate". Acta. Cryst. ***E61*** *(2): m293-m295. DOI:10.1107/S1600536805000085. (Public domain; Ben Mills).*

This physical property can be seen in the equilibrium constants for 18-crown-6 and various alkali metals:

$$Na^+_{(aq)} + C_{12}H_{24}O_{6\ (aq)} \rightarrow Na{-}crown^+_{(aq)}$$

K = 6.6

$$K^+_{(aq)} + C_{12}H_{24}O_{6\ (aq)} \rightarrow K{-}crown^+_{(aq)}$$

K = 111.6

$$Rb^+_{(aq)} + C_{12}H_{24}O_{6\ (aq)} \rightarrow Rb{-}crown^+_{(aq)}$$

K = 36

If an aqueous solution is made that is 0.006 M in both 18-crown-6 and Rb^+, what is the concentration of unbound Rb^+ at equilibrium? If the same solution is made, but with K^+ instead of Rb^+ ions, what is the concentration of unbound K+ ions at equilibrium?

Answer

First, construct an ICE table.

$$Rb^+_{aq} + C_{12}H_{24}O_{6\ (aq)} \rightleftharpoons Rb{-}crown^+_{aq}$$

	Rb^+	$C_{12}H_{24}O_6$	Rb-crown+
I	0.006	0.006	0
C	-x	-x	+x

	Rb^+	$C_{12}H_{24}O_6$	Rb-crown+
E	0.006-x	0.006-x	x

Then, use the K value of the reaction to solve for x. Use x to solve for the concentration of the desired ion.

$$K = \frac{[Rb-crown+]}{[Rb+][C_{12}H_{24}O_6]}$$

$$36 = \frac{[x]}{[0.006-x][0.006-x]}$$

$$x = 9.2954 \times 10^{-4}$$

$$[Rb^+] = 0.0507M$$

Repeat this process for the other reaction.

$$K^+_{aq} + C_{12}H_{24}O_{6\,(aq)} \rightleftharpoons K-crown^+_{aq}$$

	K^+	$C_{12}H_{24}O_6$	**K-crown+**
I	0.006	0.006	0
C	-x	-x	+x
E	0.006-x	0.006-x	x

$$K = \frac{[K-crown^+]}{[K^+][C_{12}H_{24}O_6]}$$

$$111.6 = \frac{[x]}{[0.006-x][0.006-x]}$$

$$x = 0.0019$$

$$[K^+] = 0.0041M$$

Q39

Is it easier to dissolve CuBr into 1M of NaBr solution than to dissolve it into pure water? Does the answer change if when the concentration of NaBr is 0.5M?

Answer

1. When CuBr is added into NaBr solution, the common ion effect occurs. Common ion effect explains that the solvent is responsible for the decrease in the solubility of the precipitate when the soluble compound contains one of the ions of the precipitate that is added to the solution in equilibrium. According to Le Chatelier's principle, some of the ions in excess should be removed from the solution. So it is harder to dissolve CuBr into NaBr solution than dissolve it into pure water.

2. If the concentration is changed to 0.5M, it is still harder to dissolve CuBr in NaBr solution, but less difficult.

Q41

Identify the salt NH_4F as either acidic, basic, or neutral. Then explain the mechanism behind why the salt is acidic, basic, or neutral using chemical equations and their K_a or K_b values provided here and here.

Answer

- For a salt to have an acidic character, it must be able to accept OH^- ions when it dissociates in an aqueous solution and leave an excess of H^+ in the solution to have an acidic effect.
- For a salt to have a basic character, it must be able to either accept an H^+ when it dissociates in an aqueous solution and leave an excess of OH^- in the solution to have an basic effect.

NH_4F can be classified as either acidic or basic depending upon which species is present in a greater concentration (H^+ or OH^-) in the solution when NH_4F is added.

$$NH^+_{4\,(aq)} + F^-_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3\,(aq)} + HF_{(aq)} + H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$Ka{=}5 \cdot 6 \times 10^{-10} \text{ for } NH^+_{4\,(aq)} + H_2O_{(1)} \rightleftharpoons NH_{3\,(aq)} + H_3O^+_{(aq)}$$

$$Kb{=}1 \cdot 6 \times 10^{-11} \text{ for } F^-_{(aq)} + H_2O_{(1)} \rightleftharpoons HF_{(aq)} + OH^-_{(aq)}$$

Since $K_a > K_b$, NH_4^+ has a greater affect on the solution and therefore the salt is acidic.

** See key for problem 15.23 on how to calculate K_b or K_a given K_a or K_b

Q43

For the complex ion, $Fe(H_2O)^{3+}_{6(aq)}$, the acid ionization constant for 298K is 7.7×10^{-3}. What is the pH of a 50 mL solution that contains 0.02 mols of $Fe(NO_3)_2$?

Answer

Complex ion problems are solved identically to other equilibrium problems.

First, write the balanced equation:

$$[Fe(H_2O)_6]^{3+}_{(aq)} + H_2O_{(aq)} \rightleftharpoons [Fe(H_2O)_5OH]^{2+}_{(aq)} + H_3O^+_{(aq)}$$

Then, create and solve an ICE table.

$[Fe(H_2O)_6]^{3+}$	H_2O	H_3O^{3+}	$[Fe(H_2O)_5OH]^{2+}$
0.40	-	0	0
-x	-	+x	+x
0.40-x	-	x	x

From the ICE table:

$$K_a = \frac{[H_3O^{3+}][Fe(H_2O)_5OH^{2+}]}{[Fe(H_2O)_6^{3+}]}$$

$$7.7 \times 10^{-3} = K_a = \frac{[x]\,[x]}{[0.4 - x]}$$

By rearranging the equation:

$$x^2 + 0.0077x - 0.00308 = 0$$

and using the quadratic,

$$\frac{-0.0077 \pm \sqrt{0.0077^2 - 4\,(1)\,(-0.00308)}}{2}$$

$$x = 0.05178$$

$$pH = -\log[H_3O^+] = 1.286$$

Q45

Calculate the concentration of H_3O^+ in a 0.3 M solution of oxalic acid ($pK_{a1} = 1.25; pK_{a2} = 3.81$).

Answer

$K_a = 10^{-1.25} = 0.0562$

Balanced equation:

$$C_2H_2O_4 + H_2O \rightleftharpoons C_2HO_4^- + H_3O^+$$

	$C_2H_2O_4$	$C_2HO_4^-$	H_3O^+
I	0.3	0	0
C	-x	+x	+x
E	0.3-x	x	x

At equilibrium:

$$\frac{(x)^2}{(0.3-x)} = K_{a1}$$

$$x = 0.1048$$

Balanced equation:

$$C_2HO_4^- + H_2O \rightleftharpoons C_2O_4^{2-} + H_3O^+$$

	$C_2HO_4^-$	$C_2O_4^{2-}$	H_3O^+
I	0.1048	0	0.1048
C	-x	+x	+x
E	0.1048-x	x	x+0.1048

At equilibrium:

$$K_{a2} = 10^{-3.81}$$

$$\frac{x(x+0.1048)}{(0.1048-x)} = K_{a2}$$

$$x = 0.000154$$

$$[H_3O^+] = 0.1048 + 0.000154\ M = 0.105\ M$$

Q49

An aqueous solution at 25 °C is 0.10 M in both Ba^{2+} and Ca^{2+} ions. One wants to separate the two ions by taking advantage of the different solubility of $BaCO_3$ and $CaCO_3$.

$BaCO_3\ K_{sp} = 2.58 \times 10^{-9}\ M$

$CaCO_3\ K_{sp} = 3.36 \times 10^{-9}\ M$

What is the highest possible CO_3^{2-} concentration that allows only one salt to present at equilibrium? Which ion is present in the solid, Ba^{2+} or Ca^{2+}?

Answer

$$BaCO_{3(s)} \leftrightharpoons Ba^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$

$$[CO_3^{2-}] < \frac{K_{sp}}{[Ba^{2+}]} = \frac{2.58 \times 10^{-9}}{0.1\ M} = 2.58 \times 10^{-8}\ M\ (\text{Using the formula for } K_{sp})$$

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$

$$[\mathrm{CO_3^{2-}}] < \frac{\mathrm{K_{sp}}}{[\mathrm{Ca^{2+}}]} = \frac{3.36\times10^{-9}}{0.1\ \mathrm{M}} = 3.36\times10^{-8}\ \mathrm{M}$$

Therefore, the highest possible CO_3^{2-} concentration that allows only one salt to present at equilibrium is 2.58×10^{-8} M. Ba^{2+} is present in the solid.

Q51

A solution was created by dissolving 1.31 kg of $Ba(NO_3)_2$ into 1 L of 0.50 M $Ca(NO_3)_2$. Determine which molecule is more soluble. Then determine the concentration of SO_4 ion is needed to precipitate all of one molecule but leave the other molecule completely unreacted, use Table E3.

Answer

First we must determine the mass action equation for dissolving the salts:

$$\mathrm{K_{sp}} = [\mathrm{Ba^+}][\mathrm{SO_4^-}] = 1.08\times10^{-10}$$

$$\mathrm{K_{sp}} = [\mathrm{Ca^+}][\mathrm{SO_4^-}] = 4.93\times10^{-5}$$

We will use $CaSO_4$ as the salt because it is the most soluble.

For Ca^+ to to remain in solution, its reaction quotient must remain smaller than then its K_{sp}:

$$\mathrm{Q} = [\mathrm{Ca^+}][\mathrm{SO_4^-}] < 4.93\times10^{-5}$$

Now we just need to impute the concentration of Ca^+ and solve for the concentration of SO_4 ion:

$$[0.5\ \mathrm{M}][\mathrm{SO_4^-}] < 4.93\times10^{-5}$$

$$[\mathrm{SO_4^-}] < 9.86\times10^{-5}\ \mathrm{M}$$

So as long as the concentration of SO_4 ion is smaller than 9.86 x 10^{-5} M, no $CaSO_4$ will precipitate

Q55

Let's say you have a solution that is saturated with HF at a concentration of $[HF] = 0.20M$.

a. If you want some element X whose concentration is equal to 0.20 M to exist entirely in this solution, what will be the highest pH possible for this mixture? ($K_a\ of\ HF\ is\ 6.6\times10^{-4}$ and $K\ of\ XF(s) = 2.5\times10^{-16}$) . Hint: the reaction is given as $XF(s) + H_2O(l) \leftrightharpoons X(aq) + F^-(aq) + OH^-(aq)$
b. What would be the concentration of some element G in equilibrium with solid GF in this solution at the pH value found in part a) given that $K\ of\ GF(s) = 4.9\times10^{-22}$) .

Answer

Part a)

Since you have the equation $XF(s) + H_2O(l) \leftrightharpoons X(aq) + F^-(aq) + OH^-(aq)$, the equilibrium constant K will be equal to

$$K = [X]\ [F^-]\ [OH^-] = 2.5\times10^{-16}$$

We now replace these variables above with known derived equations

$$K = [X]\left(\frac{[K_a][HF]}{[H_3O^+]}\right)\left(\frac{[K_w]}{[H_3O^+]}\right) = 2.5\times10^{-16}$$

Plug in known values and solve for $[H_3O^+]$

$$[H_3O^+] = \sqrt{\frac{(0.20)\ (6.6\times10^{-4})\ (0.20)\ (1.0\times10^{-14})}{2.5\times10^{-16}}}$$

$$[H_3O^+] = 0.0325\ M$$

Now we solve for pH and see that

$$pH = -log(0.0325) = 1.50$$

Part b)

For part b), we solve the question in a very similar manner as used in part a) with the only differences being a few different variables we plug in. Now, we are solving for our concentration of some element G using the value of H_3O^+ we found above.

Given the reaction $GF(s) + H_2O(l) \leftrightharpoons G(aq) + F^-(aq) + OH^-(aq)$, the equilibirum constant K will be equal to

$$K = [G]\ [F^-]\ [OH^-] = 4.90 \times 10^{-22}$$

We now replace these variables above with known derived equations and this time, solve for $[G]$ using the $[H_3O^+]$ value found above

$$K = [G]\ (\frac{[K_a][HF]}{[H_3O^+]})\ (\frac{[K_w]}{[H_3O^+]}) = 4.9 \times 10^{-22}$$

$$[G] = 3.92 \times 10^{-7}\ M$$

Q63

200 mL of 0.5M NaCl and 800 mL of 0.10M AgNO$_3$ are mixed together. Calculate the mass of NaNO$_3$ precipitated. Assume:

- that the volumes are additive,
- that AgCl is completely insoluble, and
- any other substances that may form are completely soluble.

Answer

Because NaCl and AgNO$_3$ are strong electrolytes, they dissolve in water by dissociation.
NaNO$_3$ precipitates according to the net ionic equation

$$Na^+_{(aq)} + NO^-_{3(aq)} \rightarrow NaNO_{3(s)}$$

First calculate the moles of each ion present.

$$n_{Na^+} = 0.2L \times 0.5M = 0.1 mol Na^+$$

$$n_{NO_3^-} = 0.8L \times 0.1M = 0.08 mol NO_3^-$$

Assuming that NaNO$_3$ is completely insoluble, the reaction continues until the entire 0.08 mol of NO$_3^-$ is consumed, which is the limiting reactant, creating 0.08 mol NaNO$_3$.

$$0.08\ mol\ NaNO_3(84.99\frac{g}{mol}) = 6.80\ g\ NaNO_3$$

Q69

Siobhan has a $1L$ solution with containing $0.050M$ of $CO^{2-}_{3\ (aq)}$ and $0.100M$ of $F^-_{(aq)}$. She titrates the solution with a 0.100 M titrand of Iron Iodide, FeI_2. The K_{sp} expressions are:

$$FeCO_{3\ (s)} \rightleftharpoons CO^{2-}_{3\ (aq)} + Fe^{2+}_{(aq)}\ \ K_{sp} = 3.13 \times 10^{-11}$$

$$FeF_{2\ (s)} \rightleftharpoons 2F^-_{(aq)} + Fe^{2+}_{(aq)}\ \ K_{sp} = 2.36 \times 10^{-6}$$

At what volume of iron iodide will the precipitate $FeCO_{3\ (s)}$ appear? How about $FeF_{2\ (s)}$?

Answer

This problem primarily focuses on expanding on how the solubility constant K_{sp} can predict which solution will titrate first. When Iron Iodide is dripped into the solution, it disassociates into Iron(II) and Iodide Ions.

$$FeI_2 \rightarrow Fe^{2+}_{(aq)} + 2I^-_{aq}$$

This facilitates a "common ion effect", where the ions from the dissolution of the titrand Iron Iodide contribute to shifting the concentration of the other two reactions:

$$FeCO_{3\,(s)} \rightleftharpoons CO^{2-}_{3\,(aq)} + Fe^{2+}_{(aq)}$$

$$FeF_{2\,(s)} \rightleftharpoons 2F^{-}_{(aq)} + Fe^{2+}_{(aq)}$$

As seen here, the introduction of Fe^{2+} ions will mean there is a larger iron ion concentration, which shifts both of the above reactions to the left. This concept that explains this phenomena is colloquially known as Le Chatlier's principle. However, in order to precisely determine at what point precipitate will form, the K_{sp} values need to be taken into consideration. Recall that the K constant is defined in terms of either concentrations or partial pressures. As the species in this problem are only aqueous solutes and not gaseous compounds, the resulting K_{sp} will be defined by concentrations as depicted below:

$$FeCO_{3\,(s)} \rightleftharpoons CO^{2-}_{3\,(aq)} + Fe^{2+}_{(aq)} \quad K_{sp} = \frac{\left[CO_3^{2-}\right]\left[Fe^{2+}\right]}{1} = 3.13 \times 10^{-11}$$

$$FeF_{2\,(s)} \rightleftharpoons 2F^{-}_{(aq)} + Fe^{2+}_{(aq)} \quad K_{sp} = \frac{\left[F^{-}\right]^2\left[Fe^{2+}\right]}{1} = 2.36 \times 10^{-6}$$

Notice that each K_{sp} is divided by 1. This is to represent the solid reactants. Also, based on the information above, recognize that, at equilibrium, the product of the concentrations of the two ions should equal to thier K_{sp}, and since the problem provided both $\left[CO_3^{2+}\right]$ and $\left[F^{-}\right]$. By substituting these concentrations into the respective K_{sp} formulas, the equations can be algebraically manipulated to provide the $\left[Fe^{2+}\right]$ at equilibrium. This process is seen below for $FeF_{2\,s}$. The process is basically the same to finding $\left[Fe^{2+}\right]$ for $\left[CO_3^{2+}\right]$, but there is no need to square root the value since there is no stoichiometric coefficients for that particular equation. In contrast, F^{-} has a stoichiometric coefficient of 2). Since only initial concentrations were given, we can determine at which point $Q_{sp} > K_{sp}$

$$Q_{sp} = \frac{\left[F^{-}\right]^2\left[Fe^{2+}\right]}{1} = 2.36 \times 10^{-6}$$

$$Q_{sp} = (0.05M)^2\left[Fe^{2+}\right] = 2.36 \times 10^{-6}$$

$$\left[Fe^{2+}\right] = \frac{2.36 \times 10^{-6}}{(0.100M^2)} = 2.36 \times 10^{-4} M$$

$$\text{Therefore, } \left[Fe^{2+}\right] \text{ for } FeF_2 = 2.36 \times 10^{-4} M$$

$$\text{And } \left[Fe^{2+}\right] \text{ for } FeCO_3 = 6.26 \times 10^{-10} M \text{, using the same method.}$$

What this information tells us is the calculated $\left[Fe^{2+}\right]$ is the concentration of Fe^{2+} that one would expect to be in equilibrium at the given concentration of the other ion. Therefore, if $\left[Fe^{2+}\right]$ is higher than this value, then the resulting reaction quotient will be larger than K_{sp}, causing the reaction to shift towards the product and consequently causing the precipitate to form. From the values, it is clear that $FeCO_{3\,(s)}$ will end up precipitating first, and then $FeF_{2\,s}$.

Finding the exact volume that the precipitate for each reaction will form is relatively straightforward. Based on the information overviewed before, after the $\left[Fe^{2+}\right]$ reaches the calculated point, precipitate will form. Therefore, to find the volume of titrant needed, just set up the following equation:

$$molarity_{titrant} \times V_{titrant} = mol_{titrant} = mol_{Fe^{2+} to precipitate}$$

$$0.100M \times V_{titrant} = \left(6.26 \times 10^{-10} M\right)(1L)$$

$$0.100M \times V_{titrant} = 6.26 \times 10^{-10} mol$$

$$V_{titrant} = \frac{6.26 \times 10^{10} mol}{0.100M}$$

$$V_{titrant} = 6.26 \times 10^{-9} L \text{ for } FeCO_{3\,(s)} \text{ precipitate to form.}$$

Via the same process, $V_{titrant} = 0.00236L$for $FeF_{2\,(s)}$ to form.

Abstract: Use K_{sp} to determine Q_{sp} concentration $\left[Fe^{2+}\right]$. Divide by molarity of titrant to get desired volume for precipitate to form.

Q73

Complex ion plays an important role in the level of solubility. For example:

$$Hg^{2+}_{(aq)} + 2I^-_{(aq)} \rightleftharpoons HgI_{2(s)}$$

This reaction results in the formation of solid HgI_2. However, when solid HgI_2 reacts in the same process:

$$HgI_{2(s)} + I^-_{(aq)} \rightleftharpoons HgI^-_{3(aq)}$$

The solubility increases greatly and the reaction results in an aqueous product. Explain this phenomenon.

Answer

The first reaction produces a solid precipitate and the second reaction is soluble because complex ions are created in the reaction. HgI_3^- is a complex ion, which means it has Hg ion in the center that is surrounded by iodine molecules that are able to act as Lewis bases and attract the protons of the Lewis acid in the reaction. These properties are brought out as a result of the reaction and result in an aqueous product.

Q73

Why does the inclusion of NH_3 increase the solubility of $CuCl_2$ in an aqueous solution?

Answer

The solubility of Cu^{2+} increases when NH_3 present because NH_3 forms a complex ion with Cu^{2+}. The corresponding the chemical reaction for is as follows,

$$\mathrm{CuCl_{2(s)}} \rightleftharpoons \mathrm{Cu^{2+}_{(aq)}} + 2\mathrm{Cl^-_{(aq)}} + 4\mathrm{NH_{3(aq)}} \rightleftharpoons [\mathrm{Cu(NH_3)_4}]^{2+}$$

The formation of the complex ion pulls equilibrium towards the right which allows more $CuCl_2$ to dissolve.

CHAPTER OVERVIEW

17: Electrochemistry

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

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XVII XVIII XIX XX XXI XXII XXIII • **Homework Exercises**

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Electrochemistry is the study of electricity and how it relates to chemical reactions. In electrochemistry, electricity can be generated by movements of electrons from one element to another in a reaction known as redox reaction, or oxidation-reduction reaction.

Topic hierarchy

17.1: Electrochemical Cells

Learning Objectives

- To understand the basics of voltaic cells
- To connect voltage from a voltaic cell to underlying redox chemistry

In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. A redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The **reductant** is the substance that loses electrons and is oxidized in the process; the **oxidant** is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements.

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two **half-reactions**, one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

$$\mathrm{Zn(s)+Br_2(aq)\rightarrow Zn^{2\,+}(aq)+2\,Br^-(aq)}$$

The half-reactions are as follows:

reduction half-reaction:

$$\mathrm{Br_2(aq)+2\,e^-\rightarrow 2\,Br^-(aq)}$$

oxidation half-reaction:

$$\mathrm{Zn(s)\rightarrow Zn^{2\,+}(aq)+2\,e^-}$$

Each half-reaction is written to show what is actually occurring in the system; Zn is the *reductant* in this reaction (it loses electrons), and $\mathrm{Br_2}$ is the *oxidant* (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation $17.1.1$). A redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

> *In any redox reaction, the number of electrons lost by the oxidation reaction(s) equals the number of electrons gained by the reduction reaction(s).*

In most of our discussions of chemical reactions, we have assumed that the reactants are in intimate physical contact with one another. Acid–base reactions, for example, are usually carried out with the acid and the base dispersed in a single phase, such as a liquid solution. With redox reactions, however, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work. An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an **electrochemical cell**.

There are two types of electrochemical cells: galvanic cells and electrolytic cells. Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. A **galvanic (voltaic) cell** uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to generate electricity. This type of electrochemical cell is often called a voltaic cell after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an **electrolytic cell** consumes electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two **electrodes**, which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system (Figure $17.1.1$). The oxidation half-reaction occurs at one electrode (the **anode**), and the reduction half-reaction occurs at the other (the **cathode**). When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an electrolyte, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining the system's electrical neutrality. In this section, we focus on reactions that occur in galvanic cells.

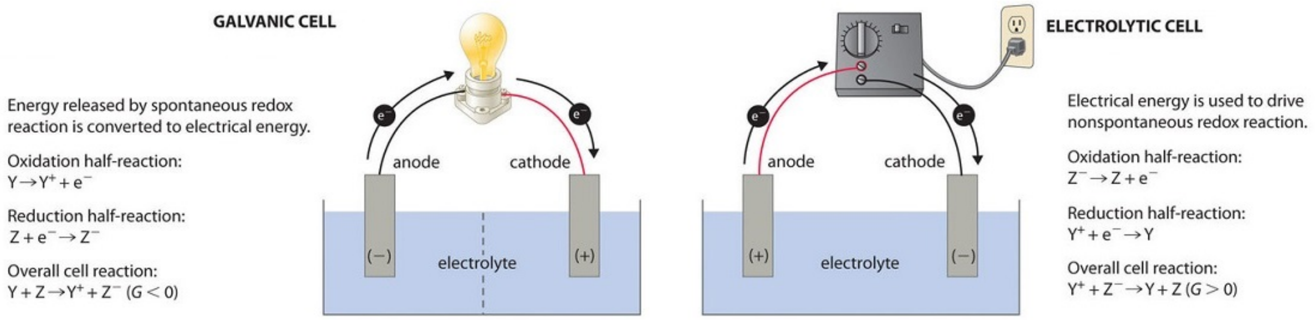


Figure 17.1.1: Electrochemical Cells. A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Voltaic (Galvanic) Cells

To illustrate the basic principles of a galvanic cell, let's consider the reaction of metallic zinc with cupric ion (Cu^{2+}) to give copper metal and Zn^{2+} ion. The balanced chemical equation is as follows:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \tag{17.1.1}$$

We can cause this reaction to occur by inserting a zinc rod into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc rod dissolves, and a mass of metallic copper forms. These changes occur spontaneously, but all the energy released is in the form of heat rather than in a form that can be used to do work.

Figure 17.1.2: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment. When a zinc rod is inserted into a beaker that contains an aqueous solution of copper(II) sulfate, a spontaneous redox reaction occurs: the zinc electrode dissolves to give $Zn^{2+}(aq)$ ions, while $Cu^{2+}(aq)$ ions are simultaneously reduced to metallic copper. The reaction occurs so rapidly that the copper is deposited as very fine particles that appear black, rather than the usual reddish color of copper. (youtu.be/2gPRK0HmYu4)

This same reaction can be carried out using the galvanic cell illustrated in Figure $17.1.3a$. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of Cu^{2+} ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of Zn^{2+} ions. The two metal strips, which serve as electrodes, are connected by a wire, and the compartments are connected by a **salt bridge**, a U-shaped tube inserted into both solutions that contains a concentrated liquid or gelled electrolyte. The ions in the salt bridge are selected so that they do not interfere with the electrochemical reaction by being oxidized or reduced themselves or by forming a precipitate or complex; commonly used cations and anions are Na^+ or K^+ and NO_3^- or SO_4^{2-}, respectively. (The ions in the salt bridge do not have to be the same as those in the redox couple in either compartment.) When the circuit is closed, a spontaneous reaction occurs: zinc metal is oxidized to Zn^{2+} ions at the zinc electrode (the anode), and Cu^{2+} ions are reduced to Cu metal at the copper electrode (the cathode). As the reaction progresses, the zinc strip dissolves, and the concentration of Zn^{2+} ions in the solution increases; simultaneously, the copper strip gains mass, and the concentration of Cu^{2+} ions in the solution decreases (Figure $17.1.3b$). Thus we have carried out the same reaction as we did using a single beaker, but this time the oxidative and reductive half-reactions are physically separated from each other. The electrons that are released at the anode flow through the wire, producing an electric current. Galvanic cells therefore transform chemical energy into electrical energy that can then be used to do work.

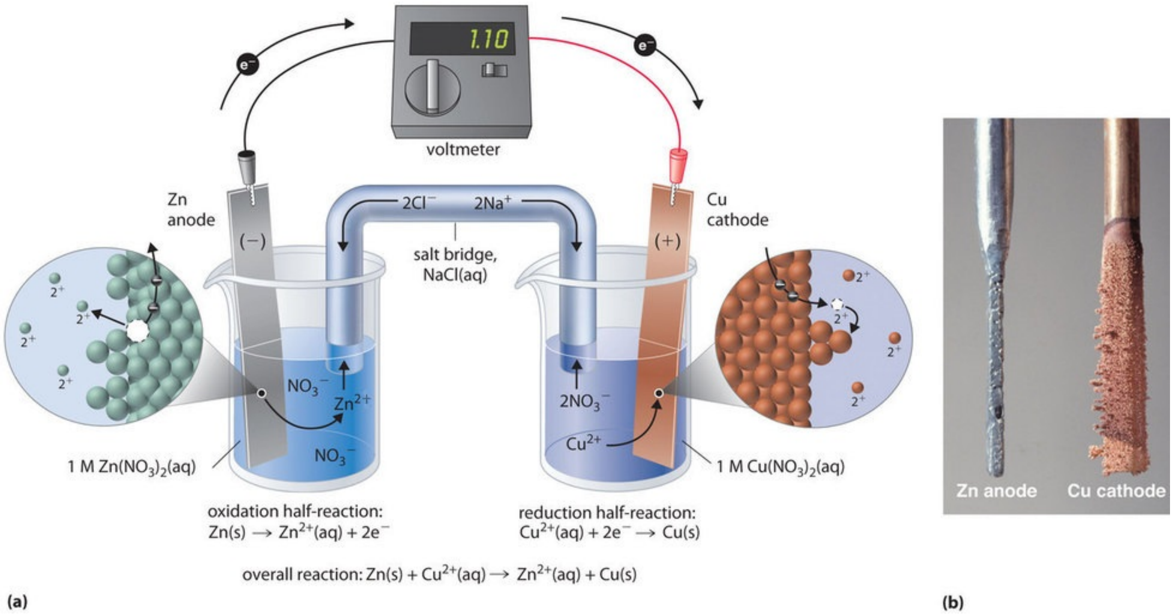


Figure 17.1.3: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell. (a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu^{2+} ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of Zn^{2+} ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to Zn^{2+} ions in the left compartment, while Cu^{2+} ions are simultaneously reduced to copper metal at the copper electrode (the cathode). (b) As the reaction progresses, the Zn anode loses mass as it dissolves to give $Zn^{2+}(aq)$ ions, while the Cu cathode gains mass as $Cu^{2+}(aq)$ ions are reduced to copper metal that is deposited on the cathode. (CC BY-SA-NC; anonymous)

The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The identity of the salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell. Without such a connection, the total positive charge in the Zn^{2+} solution would increase as the zinc metal dissolves, and the total positive charge in the Cu^{2+} solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the Zn^{2+} solution and a flow of cations into the Cu^{2+} solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.

A voltmeter can be used to measure the difference in electrical potential between the two compartments. Opening the switch that connects the wires to the anode and the cathode prevents a current from flowing, so no chemical reaction occurs. With the switch closed, however, the external circuit is closed, and an electric current can flow from the anode to the cathode. The **potential** (E_{cell}) of the cell, measured in volts, is the difference in electrical potential between the two half-reactions and is related to the energy needed to move a charged particle in an electric field. In the cell we have described, the voltmeter indicates a potential of 1.10 V (Figure $17.1.3a$). Because electrons from the oxidation half-reaction are released at the anode, the anode in a galvanic cell is negatively charged. The cathode, which attracts electrons, is positively charged.

Not all electrodes undergo a chemical transformation during a redox reaction. The electrode can be made from an inert, highly conducting metal such as platinum to prevent it from reacting during a redox process, where it does not appear in the overall electrochemical reaction. This phenomenon is illustrated in Example $17.1.1$.

> *A galvanic (voltaic) cell converts the energy released by a* ***spontaneous*** *chemical reaction to electrical energy. An electrolytic cell consumes electrical energy from an external source to drive a* ***nonspontaneous*** *chemical reaction.*

✓ Example 17.1.1

A chemist has constructed a galvanic cell consisting of two beakers. One beaker contains a strip of tin immersed in aqueous sulfuric acid, and the other contains a platinum electrode immersed in aqueous nitric acid. The two solutions are connected by a salt bridge, and the electrodes are connected by a wire. Current begins to flow, and bubbles of a gas appear at the platinum electrode. The spontaneous redox reaction that occurs is described by the following balanced chemical equation:

$$3\,\mathrm{Sn(s)} + 2\,\mathrm{NO_3^-(aq)} + 8\,\mathrm{H^+(aq)} \rightarrow 3\,\mathrm{Sn^{2+}(aq)} + 2\,\mathrm{NO(g)} + 4\,\mathrm{H_2O(l)}$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is the positive electrode and which is the negative electrode.

Given: galvanic cell and redox reaction

Asked for: half-reactions, identity of anode and cathode, and electrode assignment as positive or negative

Strategy:

A. Identify the oxidation half-reaction and the reduction half-reaction. Then identify the anode and cathode from the half-reaction that occurs at each electrode.
B. From the direction of electron flow, assign each electrode as either positive or negative.

Solution

A In the reduction half-reaction, nitrate is reduced to nitric oxide. (The nitric oxide would then react with oxygen in the air to form NO_2, with its characteristic red-brown color.) In the oxidation half-reaction, metallic tin is oxidized. The half-reactions corresponding to the actual reactions that occur in the system are as follows:

reduction:

$$\mathrm{NO_3^-(aq)} + 4\,\mathrm{H^+(aq)} + 3\,\mathrm{e^-} \rightarrow \mathrm{NO(g)} + 2\,\mathrm{H_2O(l)}$$

oxidation:

$$\mathrm{Sn(s)} \rightarrow \mathrm{Sn^{2+}(aq)} + 2\,\mathrm{e^-}$$

Thus nitrate is reduced to NO, while the tin electrode is oxidized to Sn^{2+}.

Because the reduction reaction occurs at the Pt electrode, it is the cathode. Conversely, the oxidation reaction occurs at the tin electrode, so it is the anode.

B Electrons flow from the tin electrode through the wire to the platinum electrode, where they transfer to nitrate. The electric circuit is completed by the salt bridge, which permits the diffusion of cations toward the cathode and anions toward the anode. Because electrons flow from the tin electrode, it must be electrically negative. In contrast, electrons flow toward the Pt electrode, so that electrode must be electrically positive.

? Exercise 17.1.1

Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of $\mathrm{MnO_4^-}$ in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of $\mathrm{Sn^{2+}}$ in dilute sulfuric acid, also with a Pt electrode. When the two electrodes are connected by a wire, current flows and a spontaneous reaction occurs that is described by the following balanced chemical equation:

$$2\,\mathrm{MnO_4^-(aq)} + 5\,\mathrm{Sn^{2+}(aq)} + 16\,\mathrm{H^+(aq)} \rightarrow 2\,\mathrm{Mn^{2+}(aq)} + 5\,\mathrm{Sn^{4+}(aq)} + 8\,\mathrm{H_2O(l)}$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is positive and which is negative.

Answer a

$$\mathrm{MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)}$$

$$\mathrm{Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\,e^-}$$

Answer b

The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.

Answer c

The cathode (electrode in beaker that contains the permanganate solution) is positive, and the anode (electrode in beaker that contains the tin solution) is negative.

Electrochemical Cells: Electrochemical Cells(opens in new window) [youtu.be]

Constructing Cell Diagrams (Cell Notation)

Because it is somewhat cumbersome to describe any given galvanic cell in words, a more convenient notation has been developed. In this line notation, called a cell diagram, the identity of the electrodes and the chemical contents of the compartments are indicated by their chemical formulas, with the anode written on the far left and the cathode on the far right. Phase boundaries are shown by single vertical lines, and the salt bridge, which has two phase boundaries, by a double vertical line. Thus the cell diagram for the $\mathrm{Zn/Cu}$ cell shown in Figure $17.1.3a$ is written as follows:

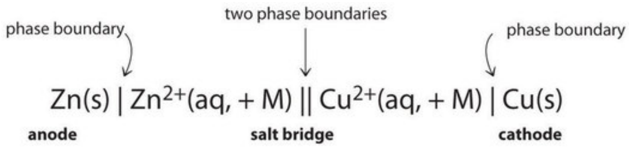


Figure 17.1.4: A cell diagram includes solution concentrations when they are provided. The + M term is meant to indicate the applicable concentration of the species. If the species is a gas, then you substitute the pressure instead.

At the anode is solid zinc. after the phase boundary is aq Zinc two plus and plus M. After the two phase boundary is aq copper two plus and plus M. At the cathode is solid copper.

Galvanic cells can have arrangements other than the examples we have seen so far. For example, the voltage produced by a redox reaction can be measured more accurately using two electrodes immersed in a single beaker containing an electrolyte that completes the circuit. This arrangement reduces errors caused by resistance to the flow of charge at a boundary, called the **junction potential**. One example of this type of galvanic cell is as follows:

$$\mathrm{Pt(s)\,|\,H_2(g)|HCl(aq,\ 1\ M)\,|\,AgCl(s)\ Ag(s)}$$

This cell diagram does not include a double vertical line representing a salt bridge because there is no salt bridge providing a junction between two dissimilar solutions. Moreover, solution concentrations have not been specified, so they are not included in the cell diagram. The half-reactions and the overall reaction for this cell are as follows:

cathode reaction:

$$\mathrm{AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)}$$

anode reaction:

$$\mathrm{\tfrac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-}$$

overall:

$$\mathrm{AgCl(s) + \tfrac{1}{2}H_2(g) \longrightarrow Ag(s) + Cl^- + H^+(aq)}$$

A single-compartment galvanic cell will initially exhibit the same voltage as a galvanic cell constructed using separate compartments, but it will discharge rapidly because of the direct reaction of the reactant at the anode with the oxidized member of the cathodic redox couple. Consequently, cells of this type are not particularly useful for producing electricity.

✓ Example 17.1.2

Draw a cell diagram for the galvanic cell described in Example $17.1.1$. The balanced chemical reaction is as follows:

$$\mathrm{3\,Sn(s) + 2\,NO_3^-(aq) + 8\,H^+(aq) \rightarrow 3\,Sn^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l)}$$

Given: galvanic cell and redox reaction

Asked for: cell diagram

Strategy:

Using the symbols described, write the cell diagram beginning with the oxidation half-reaction on the left.

Solution

The anode is the tin strip, and the cathode is the Pt electrode. Beginning on the left with the anode, we indicate the phase boundary between the electrode and the tin solution by a vertical bar. The anode compartment is thus $\mathrm{Sn(s)\,|\,Sn^{2+}(aq)}$. We could include $\mathrm{H_2SO_4(aq)}$ with the contents of the anode compartment, but the sulfate ion (as $\mathrm{HSO_4^-}$) does not participate in the overall reaction, so it does not need to be specifically indicated. The cathode compartment contains aqueous nitric acid, which does participate in the overall reaction, together with the product of the reaction (NO) and the Pt electrode. These are written as $\mathrm{HNO_3(aq)\,|\,NO(g)\,|\,Pt(s)}$, with single vertical bars indicating the phase boundaries. Combining the two compartments and using a double vertical bar to indicate the salt bridge,

$$\mathrm{Sn(s)\,|\,Sn^{2+}(aq)\,||\,HNO_3(aq)\,|\,NO(g)\,|\,Pt(s)}$$

The solution concentrations were not specified, so they are not included in this cell diagram.

? Exercise 17.1.2

Draw the cell diagram for the following reaction, assuming the concentration of $\mathrm{Ag^+}$ and $\mathrm{Mg^{2+}}$ are each 1 M:

$$\mathrm{Mg(s) + 2\,Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2\,Ag(s)}$$

Answer

$$\mathrm{Mg(s)\,|\,Mg^{2+}(aq,\ 1\ M)\,||\,Ag^+(aq,\ 1\ M)\,|\,Ag(s)}$$

Cell Diagrams: Cell Diagrams(opens in new window) [youtu.be]

Summary

A galvanic (voltaic) cell uses the energy released during a spontaneous redox reaction to generate electricity, whereas an electrolytic cell consumes electrical energy from an external source to force a reaction to occur. Electrochemistry is the study of the relationship between electricity and chemical reactions. The oxidation–reduction reaction that occurs during an electrochemical process consists of two half-reactions, one representing the oxidation process and one the reduction process. The sum of the half-reactions gives the overall chemical reaction. The overall redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. An electric current is produced from the flow of electrons from the reductant to the oxidant. An electrochemical cell can either generate electricity from a spontaneous redox reaction or consume electricity to drive a nonspontaneous reaction. In a galvanic (voltaic) cell, the energy from a spontaneous reaction generates electricity, whereas in an electrolytic cell, electrical energy is consumed to drive a nonspontaneous redox reaction. Both types of cells use two electrodes that provide an electrical connection between systems that are separated in space. The oxidative half-reaction occurs at the anode, and the reductive half-reaction occurs at the cathode. A salt bridge connects the separated solutions, allowing ions to migrate to either solution to ensure the system's electrical neutrality. A voltmeter is a device that measures the flow of electric current between two half-reactions. The potential of a cell, measured in volts, is the energy needed to move a charged particle in an electric field. An electrochemical cell can be described using line notation called a cell diagram, in which vertical lines indicate phase boundaries and the location of the salt bridge. Resistance to the flow of charge at a boundary is called the junction potential.

17.2: The Gibbs Free Energy and Cell Voltage

Learning Objectives

- To understand the relationship between cell potential and the equilibrium constant.
- To use cell potentials to calculate solution concentrations.

Changes in reaction conditions can have a tremendous effect on the course of a redox reaction. For example, under standard conditions, the reaction of $\mathrm{Co(s)}$ with $\mathrm{Ni^{2+}(aq)}$ to form $\mathrm{Ni(s)}$ and $\mathrm{Co^{2+}(aq)}$ occurs spontaneously, but if we reduce the concentration of $\mathrm{Ni^{2+}}$ by a factor of 100, so that $[\mathrm{Ni^{2+}}]$ is 0.01 M, then the reverse reaction occurs spontaneously instead. The relationship between voltage and concentration is one of the factors that must be understood to predict whether a reaction will be spontaneous.

The Relationship between Cell Potential & Gibbs Energy

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the amount of energy available to do electrical work, depends on both the cell potential and the total number of electrons that are transferred from the reductant to the oxidant during the course of a reaction. The resulting electric current is measured in **coulombs (C)**, an SI unit that measures the number of electrons passing a given point in 1 s. A coulomb relates energy (in joules) to electrical potential (in volts). Electric current is measured in **amperes (A)**; 1 A is defined as the flow of 1 C/s past a given point (1 C = 1 A·s):

$$\frac{1\ \mathrm{J}}{1\ \mathrm{V}} = 1\ \mathrm{C} = \mathrm{A} \cdot \mathrm{s}$$

In chemical reactions, however, we need to relate the coulomb to the charge on a mole of electrons. Multiplying the charge on the electron by Avogadro's number gives us the charge on 1 mol of electrons, which is called the **faraday (F)**, named after the English physicist and chemist Michael Faraday (1791–1867):

$$\begin{aligned} F &= (1.60218 \times 10^{-19}\ \mathrm{C}) \left(\frac{6.02214 \times 10^{23}\ J}{1\ \mathrm{mol\ e^-}} \right) \\ &= 9.64833212 \times 10^4\ \mathrm{C/mol\ e^-} \\ &\simeq 96,485\ J/(\mathrm{V \cdot mol\ e^-}) \end{aligned}$$

The total charge transferred from the reductant to the oxidant is therefore nF, where n is the number of moles of electrons.

Michael Faraday (1791–1867)

Faraday was a British physicist and chemist who was arguably one of the greatest experimental scientists in history. The son of a blacksmith, Faraday was self-educated and became an apprentice bookbinder at age 14 before turning to science. His experiments in electricity and magnetism made electricity a routine tool in science and led to both the electric motor and the electric generator. He discovered the phenomenon of electrolysis and laid the foundations of electrochemistry. In fact, most of the specialized terms introduced in this chapter (electrode, anode, cathode, and so forth) are due to Faraday. In addition, he discovered benzene and invented the system of oxidation state numbers that we use today. Faraday is probably best known for "The Chemical History of a Candle," a series of public lectures on the chemistry and physics of flames.

The maximum amount of work that can be produced by an electrochemical cell (w_{max}) is equal to the product of the cell potential (E°_{cell}) and the total charge transferred during the reaction (nF):

$$w_{max} = nFE_{cell}$$

Work is expressed as a negative number because work is being done by a system (an electrochemical cell with a positive potential) on its surroundings.

The change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG; this relationship is as follows:

$$\Delta G = -nFE_{cell}$$

A spontaneous redox reaction is therefore characterized by a negative value of ΔG and a positive value of E°_{cell}, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} is as follows:

$$\Delta G^{\circ} = -nFE^{\circ}_{cell} \tag{17.2.1}$$

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of E°$_{\text{cell}}$.

✓ Example 17.2.1

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in Table P2, calculate the free-energy change (ΔG°) for this redox reaction under standard conditions. Is the reaction spontaneous?

Given: redox reaction

Asked for: ΔG^{o} for the reaction and spontaneity

Strategy:

A. From the relevant half-reactions and the corresponding values of E^{o}, write the overall reaction and calculate E°_{cell}.
B. Determine the number of electrons transferred in the overall reaction. Then use Equation 17.2.1 to calculate ΔG^{o}. If ΔG^{o} is negative, then the reaction is spontaneous.

Solution

A

As always, the first step is to write the relevant half-reactions and use them to obtain the overall reaction and the magnitude of E^{o}. From Table P2, we can find the reduction and oxidation half-reactions and corresponding E^{o} values:

$$\begin{array}{lll} \text{cathode:} & \mathrm{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)} & E^{\circ}_{\text{cathode}} = 1.36\text{ V} \\ \text{anode:} & \mathrm{2Br^-(aq) \rightarrow Br_2(aq) + 2e^-} & E^{\circ}_{\text{anode}} = 1.09\text{ V} \end{array}$$

To obtain the overall balanced chemical equation, we must multiply both sides of the oxidation half-reaction by 3 to obtain the same number of electrons as in the reduction half-reaction, remembering that the magnitude of E^{o} is not affected:

$$\begin{array}{lll} \text{cathode:} & \mathrm{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)} & E^{\circ}_{\text{cathode}} = 1.36\text{ V} \\ \text{anode:} & \mathrm{6Br^-(aq) \rightarrow 3Br_2(aq) + 6e^-} & E^{\circ}_{\text{anode}} = 1.09\text{ V} \\ \hline \text{overall:} & \mathrm{Cr_2O_7^{2-}(aq) + 6Br^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Br_2(aq) + 7H_2O(l)} & E^{\circ}_{\text{cell}} = 0.27\text{ V} \end{array}$$

B

We can now calculate ΔG° using Equation 17.2.1. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\begin{aligned} \Delta G^{\circ} &= -(n)(F)(E^{\circ}_{\text{cell}}) \\ &= -(6\text{ mole})[96,485\text{ J}/(\text{V}\cdot\text{mol})(0.27\text{ V})] \\ &= -15.6\ \times 10^4\text{ J} \\ &= -156\text{ kJ/mol }\mathrm{Cr_2O_7^{2-}} \end{aligned}$$

Thus ΔG^{o} is −168 kJ/mol for the reaction as written, and the reaction is spontaneous.

? Exercise 17.2.1

Use the data in Table P2 to calculate ΔG^{o} for the reduction of ferric ion by iodide:

$$\mathrm{2\,Fe^{3+}(aq) + 2\,I^-(aq) \rightarrow 2\,Fe^{2+}(aq) + I_2(s)}$$

> Is the reaction spontaneous?
>
> **Answer**
>
> −44 kJ/mol I_2; yes

Potentials for the Sums of Half-Reactions

Although Table P2 list several half-reactions, many more are known. When the standard potential for a half-reaction is not available, we can use relationships between standard potentials and free energy to obtain the potential of any other half-reaction that can be written as the sum of two or more half-reactions whose standard potentials are available. For example, the potential for the reduction of $\mathrm{Fe^{3+}(aq)}$ to $\mathrm{Fe(s)}$ is not listed in the table, but two related reductions are given:

$$\mathrm{Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)} \quad E^\circ = +0.77 V$$

$$\mathrm{Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)} \quad E^\circ = -0.45 V$$

Although the sum of these two half-reactions gives the desired half-reaction, we cannot simply add the potentials of two reductive half-reactions to obtain the potential of a third reductive half-reaction because E^o is not a state function. However, because ΔG^o is a state function, the sum of the ΔG^o values for the individual reactions gives us ΔG^o for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. To obtain the value of E^o for the overall half-reaction, we first must add the values of $\Delta G^o (= -nFE^o)$ for each individual half-reaction to obtain ΔG^o for the overall half-reaction:

$$\begin{aligned} \mathrm{Fe^{3+}(aq) + e^-} &\rightarrow \mathrm{Fe^{2+}(aq)} & \Delta G^\circ &= -(1)(F)(0.77\ \mathrm{V}) \\ \mathrm{Fe^{2+}(aq) + 2\,e^-} &\rightarrow \mathrm{Fe(s)} & \Delta G^\circ &= -(2)(F)(-0.45\ \mathrm{V}) \\ \mathrm{Fe^{3+}(aq) + 3\,e^-} &\rightarrow \mathrm{Fe(s)} & \Delta G^\circ &= [-(1)(F)(0.77\ \mathrm{V})] + [-(2)(F)(-0.45\ \mathrm{V})] \end{aligned}$$

Solving the last expression for ΔG° for the overall half-reaction,

$$\Delta G^\circ = F[(-0.77 V) + (-2)(-0.45 V)] = F(0.13 V)$$

Three electrons ($n = 3$) are transferred in the overall reaction, so substituting into Equation 17.2.1 and solving for E^o gives the following:

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ_{\mathrm{cell}} \\ F(0.13\ \mathrm{V}) &= -(3)(F)(E^\circ_{\mathrm{cell}}) \\ E^\circ &= -\frac{0.13\ \mathrm{V}}{3} = -0.043\ \mathrm{V} \end{aligned}$$

This value of E^o is very different from the value that is obtained by simply adding the potentials for the two half-reactions (0.32 V) and even has the opposite sign.

> *Values of E^o for half-reactions cannot be added to give E^o for the sum of the half-reactions; only values of $\Delta G^o = -nFE^\circ_{cell}$ for half-reactions can be added.*

The Relationship between Cell Potential & the Equilibrium Constant

We can use the relationship between ΔG° and the equilibrium constant K, to obtain a relationship between E°_{cell} and K. Recall that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free-energy change and the equilibrium constant are related by the following equation:

$$\Delta G^\circ = -RT \ln K$$

Given the relationship between the standard free-energy change and the standard cell potential (Equation 17.2.1), we can write

$$-nFE^\circ_{cell} = -RT \ln K$$

Rearranging this equation,

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right)\ln K \tag{17.2.2}$$

For $T = 298\ K$, Equation 17.2.2 can be simplified as follows:

$$\begin{aligned} E^\circ_{\text{cell}} &= \left(\frac{RT}{nF}\right)\ln K \\ &= \left[\frac{[8.314\ \text{J}/(\text{mol}\cdot\text{K})(298\ \text{K})]}{n[96,485\ \text{J}/(\text{V}\cdot\text{mol})]}\right] 2.303\log K \\ &= \left(\frac{0.0592\ \text{V}}{n}\right)\log K \end{aligned} \tag{17.2.3}$$

Thus E°_{cell} is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of E°_{cell} and vice versa.

✓ Example 17.2.2

Use the data in Table P2 to calculate the equilibrium constant for the reaction of metallic lead with PbO_2 in the presence of sulfate ions to give $PbSO_4$ under standard conditions. (This reaction occurs when a car battery is discharged.) Report your answer to two significant figures.

Given: redox reaction

Asked for: K

Strategy:

A. Write the relevant half-reactions and potentials. From these, obtain the overall reaction and E^o_{cell}.
B. Determine the number of electrons transferred in the overall reaction. Use Equation 17.2.3 to solve for log K and then K.

Solution

A The relevant half-reactions and potentials from Table P2 are as follows:

$$\begin{array}{lll} \text{cathode:} & \mathrm{PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)} & E^\circ_{\text{cathode}} = 1.69\ \text{V} \\ \text{anode:} & \mathrm{Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-} & E^\circ_{\text{anode}} = -0.36\ \text{V} \\ \hline \text{overall:} & \mathrm{Pb(s) + PbO_2(s) + 2SO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)} & E^\circ_{\text{cell}} = 2.05\ \text{V} \end{array}$$

B Two electrons are transferred in the overall reaction, so $n = 2$. Solving Equation 17.2.3 for log K and inserting the values of n and E^o,

$$\begin{aligned} \log K &= \frac{nE^\circ}{0.0591\ \text{V}} = \frac{2(2.05\ \text{V})}{0.0591\ \text{V}} = 69.37 \\ K &= 2.3 \times 10^{69} \end{aligned}$$

Thus the equilibrium lies far to the right, favoring a discharged battery (as anyone who has ever tried unsuccessfully to start a car after letting it sit for a long time will know).

? Exercise 17.2.2

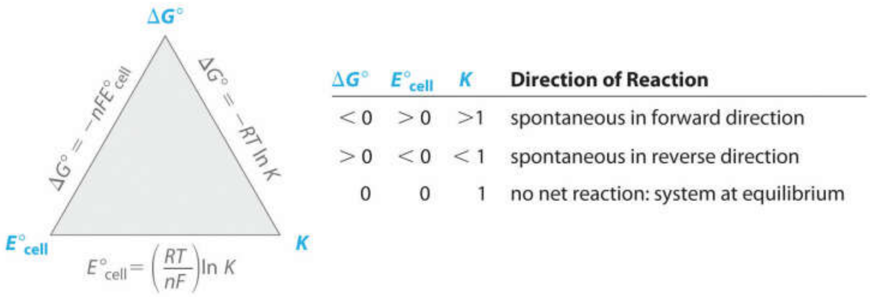
Use the data in Table P2 to calculate the equilibrium constant for the reaction of $Sn^{2+}(aq)$ with oxygen to produce $Sn^{4+}(aq)$ and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

$$2\,\mathrm{Sn^{2+}(aq) + O_2(g) + 4\,H^+(aq) \rightleftharpoons 2\,Sn^{4+}(aq) + 2\,H_2O(l)}$$

Answer

5.7×10^{72}

Figure 17.2.1 summarizes the relationships that we have developed based on properties of the system—that is, based on the equilibrium constant, standard free-energy change, and standard cell potential—and the criteria for spontaneity (ΔG° < 0). Unfortunately, these criteria apply only to systems in which all reactants and products are present in their standard states, a situation that is seldom encountered in the real world. A more generally useful relationship between cell potential and reactant and product concentrations, as we are about to see, uses the relationship between ΔG and the reaction quotient Q.



ΔG°	E°_{cell}	K	Direction of Reaction
< 0	> 0	> 1	spontaneous in forward direction
> 0	< 0	< 1	spontaneous in reverse direction
0	0	1	no net reaction: system at equilibrium

Figure 17.2.1: The Relationships among Criteria for Thermodynamic Spontaneity. The three properties of a system that can be used to predict the spontaneity of a redox reaction under standard conditions are K, ΔG°, and E°_{cell}. If we know the value of one of these quantities, then these relationships enable us to calculate the value of the other two. The signs of ΔG° and E°_{cell} and the magnitude of K determine the direction of spontaneous reaction under standard conditions. (CC BY-NC-SA; Anonymous by request)

If ΔG is less than zero, E^o is greater than zero and K is greater than 1 then the direction of the reaction is spontaneous in forward direction. If ΔG is greater than zero, E^o is less than zero and K is less than one then the direction of reaction is spontaneous in reverse direction. If ΔG is zero, E is zero and K is one that there is no net reaction and the system is at equilibrium .

Summary

A coulomb (C) relates electrical potential, expressed in volts, and energy, expressed in joules. The current generated from a redox reaction is measured in amperes (A), where 1 A is defined as the flow of 1 C/s past a given point. The faraday (F) is Avogadro’s number multiplied by the charge on an electron and corresponds to the charge on 1 mol of electrons. The product of the cell potential and the total charge is the maximum amount of energy available to do work, which is related to the change in free energy that occurs during the chemical process. Adding together the ΔG values for the half-reactions gives ΔG for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. Spontaneous redox reactions have a negative ΔG and therefore a positive E_{cell}. Because the equilibrium constant K is related to ΔG, E°_{cell} and K are also related. Large equilibrium constants correspond to large positive values of E°.

17.3: Concentration Effects and the Nernst Equation

Learning Objectives

- Relate cell potentials to Gibbs energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants

The *Nernst Equation* enables the determination of cell potential under non-standard conditions. It relates the measured cell potential to the reaction quotient and allows the accurate determination of equilibrium constants (including solubility constants).

The Effect of Concentration on Cell Potential: The Nernst Equation

Recall that the actual free-energy change for a reaction under nonstandard conditions, ΔG, is given as follows:

$$\Delta G = \Delta G^\circ + RT\ln Q \tag{17.3.1}$$

We also know that $\Delta G = -nFE_{cell}$ (under non-standard conditions) and $\Delta G^o = -nFE^o_{cell}$ (under standard conditions). Substituting these expressions into Equation 17.3.1, we obtain

$$-nFE_{cell} = -nFE^o_{cell} + RT\ln Q \tag{17.3.2}$$

Dividing both sides of this equation by $-nF$,

$$E_\text{cell} = E^\circ_\text{cell} - \left(\dfrac{RT}{nF}\right)\ln Q \tag{17.3.3}$$

Equation 17.3.3 is called the **Nernst equation**, after the German physicist and chemist Walter Nernst (1864–1941), who first derived it. The Nernst equation is arguably the most important relationship in electrochemistry. When a redox reaction is at equilibrium ($\Delta G = 0$), then Equation 17.3.3 reduces to Equation 17.3.4 and 17.3.5 because $Q = K$, and there is no net transfer of electrons (i.e., E_{cell} = 0).

$$E_\text{cell} = E^\circ_\text{cell} - \left(\dfrac{RT}{nF}\right)\ln K = 0 \tag{17.3.4}$$

since

$$E^\circ_\text{cell} = \left(\dfrac{RT}{nF}\right)\ln K \tag{17.3.5}$$

Substituting the values of the constants into Equation 17.3.3 with $T = 298\, K$ and converting to base-10 logarithms give the relationship of the actual cell potential (E_{cell}), the standard cell potential (E°_{cell}), and the reactant and product concentrations at room temperature (contained in Q):

$$E_\text{cell} = E^\circ_\text{cell} - \left(\dfrac{0.0591\text{ V}}{n}\right)\log Q \tag{17.3.6}$$

The Power of the Nernst Equation

The Nernst Equation (17.3.3) can be used to determine the value of E_{cell}, and thus the direction of spontaneous reaction, for any redox reaction under any conditions.

Equation 17.3.6 allows us to calculate the potential associated with any electrochemical cell at 298 K for any combination of reactant and product concentrations under any conditions. We can therefore determine the spontaneous direction of any redox reaction under any conditions, as long as we have tabulated values for the relevant standard electrode potentials. Notice in Equation 17.3.6 that the cell potential changes by 0.0591/n V for each 10-fold change in the value of Q because log 10 = 1.

Example 17.3.1

The following reaction proceeds spontaneously under standard conditions because E°$_{cell}$ > 0 (which means that ΔG° < 0):

$$2\,\mathrm{Ce}^{4+}(\mathrm{aq}) + 2\,\mathrm{Cl}^{-}(\mathrm{aq}) \longrightarrow 2\,\mathrm{Ce}^{3+}(\mathrm{aq}) + \mathrm{Cl}_2(\mathrm{g}) \qquad E^{\circ}_{cell} = 0.25\ V$$

Calculate E_{cell} for this reaction under the following nonstandard conditions and determine whether it will occur spontaneously: [Ce^{4+}] = 0.013 M, [Ce^{3+}] = 0.60 M, [Cl^{-}] = 0.0030 M, P_{Cl_2} = 1.0 atm, and T = 25°C.

Given: balanced redox reaction, standard cell potential, and nonstandard conditions

Asked for: cell potential

Strategy:

Determine the number of electrons transferred during the redox process. Then use the Nernst equation to find the cell potential under the nonstandard conditions.

Solution

We can use the information given and the Nernst equation to calculate E$_{cell}$. Moreover, because the temperature is 25°C (298 K), we can use Equation 17.3.6 instead of Equation 17.3.3. The overall reaction involves the net transfer of two electrons:

$$2Ce^{4+}_{(aq)} + 2e^{-} \rightarrow 2Ce^{3+}_{(aq)}$$

$$2Cl^{-}_{(aq)} \rightarrow Cl_{2(g)} + 2e^{-}$$

so n = 2. Substituting the concentrations given in the problem, the partial pressure of Cl$_2$, and the value of E°$_{cell}$ into Equation 17.3.6,

$$\begin{aligned} E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0.25\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right)\log\left(\frac{[\text{Ce}^{3+}]^2 P_{\text{Cl}_2}}{[\text{Ce}^{4+}]^2[\text{Cl}^{-}]^2}\right) \\ &= 0.25\ \text{V} - [(0.0296\ \text{V})(8.37)] = 0.00\ \text{V} \end{aligned}$$

Thus the reaction will not occur spontaneously under these conditions (because E = 0 V and ΔG = 0). The composition specified is that of an equilibrium mixture

Exercise 17.3.1

Molecular oxygen will not oxidize MnO_2 to permanganate via the reaction

$$4\,\mathrm{MnO}_2(\mathrm{s}) + 3\,\mathrm{O}_2(\mathrm{g}) + 4\,\mathrm{OH}^{-}(\mathrm{aq}) \longrightarrow 4\,\mathrm{MnO}_4^{-}(\mathrm{aq}) + 2\,\mathrm{H}_2\mathrm{O}(\mathrm{l}) \quad E^{\circ}{}_{cell} = -0.20\ V$$

Calculate E_{cell} for the reaction under the following nonstandard conditions and decide whether the reaction will occur spontaneously: pH 10, P_{O_2} = 0.20 atm, [MNO$_4^{-}$] = 1.0 × 10^{-4} M, and T = 25°C.

Answer

E$_{cell}$ = −0.22 V; the reaction will not occur spontaneously.

Applying the Nernst equation to a simple electrochemical cell such as the Zn/Cu cell allows us to see how the cell voltage varies as the reaction progresses and the concentrations of the dissolved ions change. Recall that the overall reaction for this cell is as follows:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad E^{\circ}cell = 1.10V \tag{17.3.7}$$

The reaction quotient is therefore $Q = [Zn^{2+}]/[Cu^{2+}]$. Suppose that the cell initially contains 1.0 M Cu^{2+} and 1.0 × 10^{-6} M Zn^{2+}. The initial voltage measured when the cell is connected can then be calculated from Equation 17.3.6:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\text{ V}}{n}\right)\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \tag{17.3.8}$$

$$= 1.10\text{ V} - \left(\frac{0.0591\text{ V}}{2}\right)\log\left(\frac{1.0\times10^{-6}}{1.0}\right) = 1.28\text{ V} \tag{17.3.9}$$

Thus the initial voltage is greater than E° because $Q < 1$. As the reaction proceeds, $[Zn^{2+}]$ in the anode compartment increases as the zinc electrode dissolves, while $[Cu^{2+}]$ in the cathode compartment decreases as metallic copper is deposited on the electrode. During this process, the ratio $Q = [Zn^{2+}]/[Cu^{2+}]$ steadily increases, and the cell voltage therefore steadily decreases. Eventually, $[Zn^{2+}] = [Cu^{2+}]$, so Q = 1 and $E_{cell} = E°_{cell}$. Beyond this point, $[Zn^{2+}]$ will continue to increase in the anode compartment, and $[Cu^{2+}]$ will continue to decrease in the cathode compartment. Thus the value of Q will increase further, leading to a further decrease in E_{cell}. When the concentrations in the two compartments are the opposite of the initial concentrations (i.e., 1.0 M Zn^{2+} and 1.0×10^{-6} M Cu^{2+}), $Q = 1.0 \times 10^6$, and the cell potential will be reduced to 0.92 V.

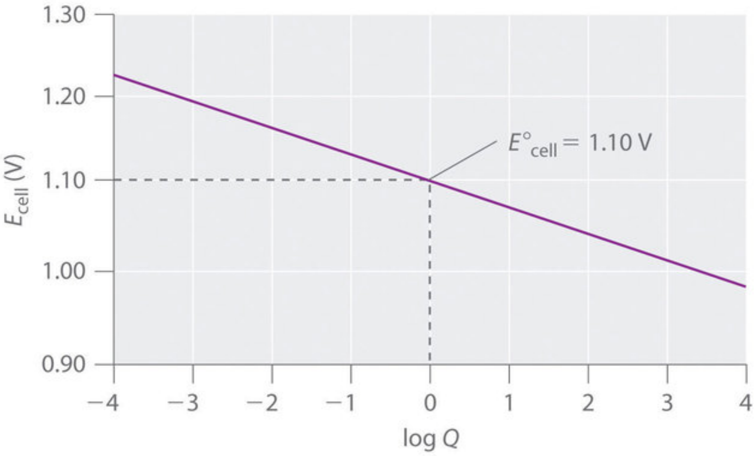


Figure 17.3.1: The Variation of E_{cell} with Log Q for a Zn/Cu Cell. Initially, log Q < 0, and the voltage of the cell is greater than $E°_{cell}$. As the reaction progresses, log Q increases, and E_{cell} decreases. When $[Zn^{2+}] = [Cu^{2+}]$, log Q = 0 and $E_{cell} = E°_{cell} = 1.10$ V. As long as the electrical circuit remains intact, the reaction will continue, and log Q will increase until Q = K and the cell voltage reaches zero. At this point, the system will have reached equilibrium.

The variation of E_{cell} with log Q over this range is linear with a slope of −0.0591/n, as illustrated in Figure 17.3.1. As the reaction proceeds still further, Q continues to increase, and E_{cell} continues to decrease. If neither of the electrodes dissolves completely, thereby breaking the electrical circuit, the cell voltage will eventually reach zero. This is the situation that occurs when a battery is “dead.” The value of Q when $E_{cell} = 0$ is calculated as follows:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\text{ V}}{n}\right)\log Q = 0 \tag{17.3.10}$$

$$E^{\circ} = \left(\frac{0.0591\text{ V}}{n}\right)\log Q \tag{17.3.11}$$

$$\log Q = \frac{E^{\circ}n}{0.0591\text{ V}} = \frac{(1.10\text{ V})(2)}{0.0591\text{ V}} = 37.23 \tag{17.3.12}$$

$$Q = 10^{37.23} = 1.7\times10^{37} \tag{17.3.13}$$

Recall that at equilibrium, $Q = K$. Thus the equilibrium constant for the reaction of Zn metal with Cu^{2+} to give Cu metal and Zn^{2+} is 1.7×10^{37} at 25°C.

The Nernst Equation: The Nernst Equation (opens in new window) [youtu.be]

Concentration Cells

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M $AgNO_3$ in one compartment and 1.0 M $AgNO_3$ in the other. The cell diagram and corresponding half-reactions are as follows:

$$\mathrm{Ag(s)} \mid \mathrm{Ag}^+(aq, 0.010\ M) \mid\mid \mathrm{Ag}^+(aq, 1.0\ M) \mid \mathrm{Ag(s)} \tag{17.3.14}$$

cathode:

$$\mathrm{Ag}^+(aq, 1.0\ M) + \mathrm{e}^- \rightarrow \mathrm{Ag(s)} \tag{17.3.15}$$

anode:

$$\mathrm{Ag(s)} \rightarrow \mathrm{Ag}^+(aq, 0.010\ M) + \mathrm{e}^- \tag{17.3.16}$$

Overall

$$\mathrm{Ag}^+(aq, 1.0\ M) \rightarrow \mathrm{Ag}^+(aq, 0.010\ M) \tag{17.3.17}$$

As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The total mass of $Ag(s)$ in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for $E°_{cell}$ because $E°_{cathode} = -E°_{anode}$:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \\ &= 0 - \left(\frac{0.0591\ \text{V}}{1}\right) \log \left(\frac{0.010}{1.0}\right) \\ &= 0.12\ \text{V} \end{aligned}$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a **concentration cell**. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two compartments will decrease, as will E_{cell}. Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero ($E_{cell} = 0$).

✓ Example 17.3.2

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of $MnCl_2$ as the cathode, and a manganese electrode immersed in a 5.2×10^{-2} M solution of $MnSO_4$ as the anode (T = 25°C).

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

A. Write the overall reaction that occurs in the cell.
B. Determine the number of electrons transferred. Substitute this value into the Nernst equation to calculate the voltage.

Solution

A This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions (Cl^- and SO_4^{2-}) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:

$$\mathrm{Mn}^{2+}(aq, 2.0\ M) \rightarrow \mathrm{Mn}^{2+}(aq, 5.2 \times 10^{-2}\ M)$$

B For the reduction of Mn^{2+}(aq) to Mn(s), n = 2. We substitute this value and the given Mn^{2+} concentrations into Equation 17.3.6:

$$\begin{aligned} E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \mathrm{V}}{n}\right) \log Q \\ &= 0\ \mathrm{V} - \left(\frac{0.0591\ \mathrm{V}}{2}\right) \log\left(\frac{5.2 \times 10^{-2}}{2.0}\right) \\ &= 0.047\ \mathrm{V} \end{aligned}$$

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

? Exercise 17.3.2

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl, and the other a 0.010 M solution of Na_2SO_4 at pH 7.00. Both cells are in contact with the atmosphere, with P_{O_2} = 0.20 atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water:

$$\mathrm{O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)}$$

What will be the potential when the circuit is closed?

Answer

0.41 V

Using Cell Potentials to Measure Solubility Products

Because voltages are relatively easy to measure accurately using a voltmeter, electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products (K_{sp}) of sparingly soluble substances. As you learned previously, solubility products can be very small, with values of less than or equal to 10^{-30}. Equilibrium constants of this magnitude are virtually impossible to measure accurately by direct methods, so we must use alternative methods that are more sensitive, such as electrochemical methods.

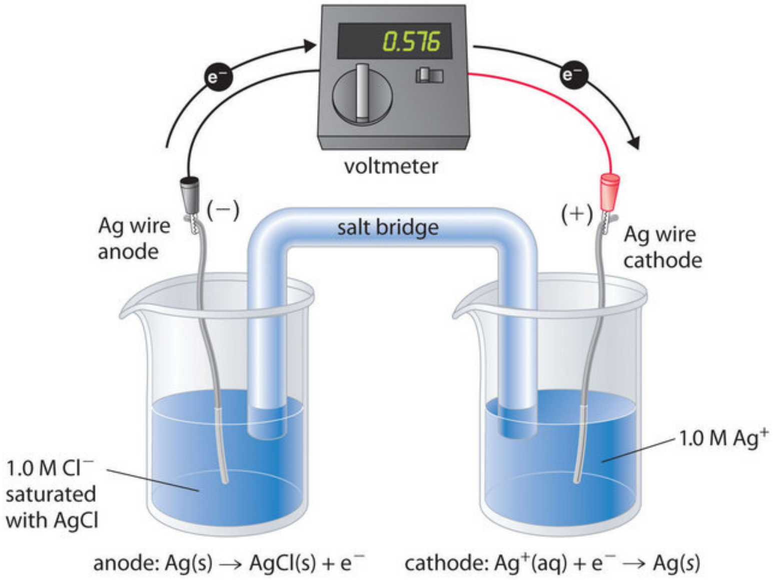


Figure 17.3.1: A Galvanic ("Concentration") Cell for Measuring the Solubility Product of AgCl. One compartment contains a silver wire inserted into a 1.0 M solution of Ag^+, and the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. The potential due to the difference in $[Ag^+]$ between the two cells can be used to determine K_{sp}. (CC BY-NC-SA; Anonymous by request)

To understand how an electrochemical cell is used to measure a solubility product, consider the cell shown in Figure 17.3.1, which is designed to measure the solubility product of silver chloride:

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-].$$

In one compartment, the cell contains a silver wire inserted into a 1.0 M solution of Ag^+; the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. In this system, the Ag^+ ion concentration in the first compartment equals K_{sp}. We can see this by dividing both sides of the equation for K_{sp} by $[Cl^-]$ and substituting:

$$\begin{aligned}[\text{Ag}^+] &= \frac{K_{sp}}{[\text{Cl}^-]} \\ &= \frac{K_{sp}}{1.0} = K_{sp}.\end{aligned}$$

The overall cell reaction is as follows:

$$\text{Ag}^+(\text{aq, concentrated}) \rightarrow \text{Ag}^+(\text{aq, dilute})$$

Thus the voltage of the concentration cell due to the difference in $[Ag^+]$ between the two cells is as follows:

$$\begin{aligned}E_{\text{cell}} &= 0\text{ V} - \left(\frac{0.0591\text{ V}}{1}\right)\log\left(\frac{[\text{Ag}^+]_{\text{dilute}}}{[\text{Ag}^+]_{\text{concentrated}}}\right) \\ &= -0.0591\text{ V }\log\left(\frac{K_{\text{sp}}}{1.0}\right) \\ &= -0.0591\text{ V }\log K_{\text{sp}} \end{aligned} \tag{17.3.18}$$

By closing the circuit, we can measure the potential caused by the difference in [Ag+] in the two cells. In this case, the experimentally measured voltage of the concentration cell at 25°C is 0.580 V. Solving Equation 17.3.18for K_{sp},

$$\begin{aligned}\log K_{\text{sp}} &= \frac{-E_{\text{cell}}}{0.0591\text{ V}} = \frac{-0.580\text{ V}}{0.0591\text{ V}} = -9.81 \\ K_{\text{sp}} &= 1.5 \times 10^{-10}\end{aligned}$$

Thus a single potential measurement can provide the information we need to determine the value of the solubility product of a sparingly soluble salt.

Example 17.3.3: Solubility of lead(II) sulfate

To measure the solubility product of lead(II) sulfate ($PbSO_4$) at 25°C, you construct a galvanic cell like the one shown in Figure 17.3.1, which contains a 1.0 M solution of a very soluble Pb^{2+} salt [lead(II) acetate trihydrate] in one compartment that is connected by a salt bridge to a 1.0 M solution of Na_2SO_4 saturated with $PbSO_4$ in the other. You then insert a Pb electrode into each compartment and close the circuit. Your voltmeter shows a voltage of 230 mV. What is K_{sp} for $PbSO_4$? Report your answer to two significant figures.

Given: galvanic cell, solution concentrations, electrodes, and voltage

Asked for: K_{sp}

Strategy:

A. From the information given, write the equation for K_{sp}. Express this equation in terms of the concentration of Pb^{2+}.
B. Determine the number of electrons transferred in the electrochemical reaction. Substitute the appropriate values into Equation ??? and solve for K_{sp}.

Solution

A You have constructed a concentration cell, with one compartment containing a 1.0 M solution of Pb^{2+} and the other containing a dilute solution of Pb^{2+} in 1.0 M Na_2SO_4. As for any concentration cell, the voltage between the two compartments can be calculated using the Nernst equation. The first step is to relate the concentration of Pb^{2+} in the dilute solution to K_{sp}:

$$\begin{aligned}[\mathrm{Pb^{2+}}][\mathrm{SO_4^{2-}}] &= K_{\mathrm{sp}}\\ [\mathrm{Pb^{2+}}] &= \frac{K_{\mathrm{sp}}}{[\mathrm{SO_4^{2-}}]} = \frac{K_{\mathrm{sp}}}{1.0\text{ M}} = K_{\mathrm{sp}}\end{aligned}$$

B The reduction of Pb^{2+} to Pb is a two-electron process and proceeds according to the following reaction:

$$Pb^{2+}(aq,\ concentrated) \rightarrow Pb^{2+}(aq,\ dilute)$$

so

$$\begin{aligned}E_{\mathrm{cell}} &= E^{\circ}_{\mathrm{cell}} - \left(\frac{0.0591}{n}\right)\log Q\\ 0.230\text{ V} &= 0\text{ V} - \left(\frac{0.0591\text{ V}}{2}\right)\log\left(\frac{[\mathrm{Pb^{2+}}]_{\mathrm{dilute}}}{[\mathrm{Pb^{2+}}]_{\mathrm{concentrated}}}\right) = -0.0296\text{ V}\log\left(\frac{K_{\mathrm{sp}}}{1.0}\right)\\ -7.77 &= \log K_{\mathrm{sp}}\\ 1.7\times 10^{-8} &= K_{\mathrm{sp}}\end{aligned}$$

Exercise 17.3.3

A concentration cell similar to the one described in Example 17.3.3 contains a 1.0 M solution of lanthanum nitrate $[La(NO_3)_3]$ in one compartment and a 1.0 M solution of sodium fluoride saturated with LaF_3 in the other. A metallic La strip is inserted into each compartment, and the circuit is closed. The measured potential is 0.32 V. What is the K_{sp} for LaF_3? Report your answer to two significant figures.

Answer

5.7×10^{-17}

Using Cell Potentials to Measure Concentrations

Another use for the Nernst equation is to calculate the concentration of a species given a measured potential and the concentrations of all the other species. We saw an example of this in Example 17.3.3, in which the experimental conditions were defined in such a way that the concentration of the metal ion was equal to K_{sp}. Potential measurements can be used to obtain the concentrations of dissolved species under other conditions as well, which explains the widespread use of electrochemical cells in many analytical devices. Perhaps the most common application is in the determination of $[H^+]$ using a pH meter, as illustrated below.

✓ Example 17.3.4: Measuring pH

Suppose a galvanic cell is constructed with a standard Zn/Zn^{2+} couple in one compartment and a modified hydrogen electrode in the second compartment. The pressure of hydrogen gas is 1.0 atm, but [H^+] in the second compartment is unknown. The cell diagram is as follows:

$$\mathrm{Zn(s)|Zn^{2+}}(aq, 1.0\,M)||\mathrm{H^+}(aq, ?\,M)|\mathrm{H_2}(g, 1.0\,atm)|Pt(s)$$

What is the pH of the solution in the second compartment if the measured potential in the cell is 0.26 V at 25°C?

Given: galvanic cell, cell diagram, and cell potential

Asked for: pH of the solution

Strategy:

A. Write the overall cell reaction.
B. Substitute appropriate values into the Nernst equation and solve for −log[H^+] to obtain the pH.

Solution

A Under standard conditions, the overall reaction that occurs is the reduction of protons by zinc to give H_2 (note that Zn lies below H_2 in Table P2):

$$\mathrm{Zn(s) + 2H^{2+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g)} \quad E° = 0.76\ \mathrm{V}$$

B By substituting the given values into the simplified Nernst equation (Equation 17.3.6), we can calculate [H^+] under nonstandard conditions:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log\left(\frac{[\mathrm{Zn^{2+}}]P_{\mathrm{H_2}}}{[\mathrm{H^+}]^2}\right) \\ 0.26\ \text{V} &= 0.76\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right)\log\left(\frac{(1.0)(1.0)}{[\mathrm{H^+}]^2}\right) \\ 16.9 &= \log\left(\frac{1}{[\mathrm{H^+}]^2}\right) = \log[\mathrm{H^+}]^{-2} = (-2)\log[\mathrm{H^+}] \\ 8.46 &= -\log[\mathrm{H^+}] \\ 8.5 &= \mathrm{pH} \end{aligned}$$

Thus the potential of a galvanic cell can be used to measure the pH of a solution.

? Exercise 17.3.4

Suppose you work for an environmental laboratory and you want to use an electrochemical method to measure the concentration of Pb^{2+} in groundwater. You construct a galvanic cell using a standard oxygen electrode in one compartment ($E°_{cathode}$ = 1.23 V). The other compartment contains a strip of lead in a sample of groundwater to which you have added sufficient acetic acid, a weak organic acid, to ensure electrical conductivity. The cell diagram is as follows:

$$Pb_{(s)} \mid Pb^{2+}(aq, ?M) \parallel H^+(aq), 1.0M \mid O_2(g, 1.0atm) \mid Pt_{(s)}$$

When the circuit is closed, the cell has a measured potential of 1.62 V. Use Table P2 to determine the concentration of Pb^{2+} in the groundwater.

Answer

$1.2 \times 10^{-9}\ M$

Summary

The Nernst equation can be used to determine the direction of spontaneous reaction for any redox reaction in aqueous solution. The Nernst equation allows us to determine the spontaneous direction of any redox reaction under any reaction conditions from values of the relevant standard electrode potentials. Concentration cells consist of anode and cathode compartments that are identical except for the concentrations of the reactant. Because ΔG = 0 at equilibrium, the measured potential of a concentration cell is zero at equilibrium (the concentrations are equal). A galvanic cell can also be used to measure the solubility product of a sparingly soluble substance and calculate the concentration of a species given a measured potential and the concentrations of all the other species.

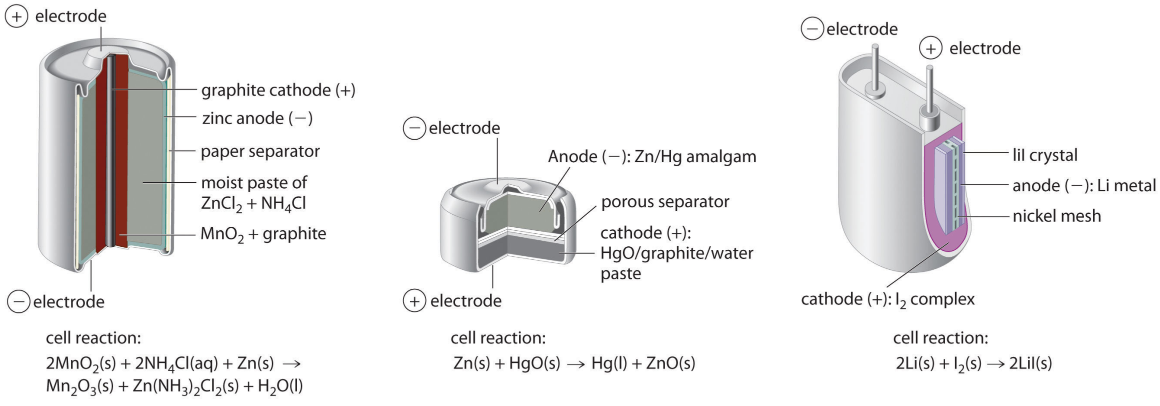
17.4: Batteries and Fuel Cells

Because galvanic cells can be self-contained and portable, they can be used as batteries and fuel cells. A **battery (storage cell)** is a galvanic cell (or a series of galvanic cells) that contains all the reactants needed to produce electricity. In contrast, a **fuel cell** is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. In this section, we describe the chemistry behind some of the more common types of batteries and fuel cells.

Batteries

There are two basic kinds of batteries: disposable, or primary, batteries, in which the electrode reactions are effectively irreversible and which cannot be recharged; and rechargeable, or secondary, batteries, which form an insoluble product that adheres to the electrodes. These batteries can be recharged by applying an electrical potential in the reverse direction. The recharging process temporarily converts a rechargeable battery from a galvanic cell to an electrolytic cell.

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. The major difference between batteries and the galvanic cells we have previously described is that commercial batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. The use of highly concentrated or solid reactants has another beneficial effect: the concentrations of the reactants and the products do not change greatly as the battery is discharged; consequently, the output voltage remains remarkably constant during the discharge process. This behavior is in contrast to that of the Zn/Cu cell, whose output decreases logarithmically as the reaction proceeds (Figure 17.4.1). When a battery consists of more than one galvanic cell, the cells are usually connected in series—that is, with the positive (+) terminal of one cell connected to the negative (−) terminal of the next, and so forth. The overall voltage of the battery is therefore the sum of the voltages of the individual cells.



(a) Leclanché dry cell **(b) Button battery** **(c) Lithium-iodine battery**

Figure 17.4.1: Three Kinds of Primary (Nonrechargeable) Batteries. (a) A Leclanché dry cell is actually a "wet cell," in which the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in producing electrical energy and has a limited shelf life. (b) In a button battery, the anode is a zinc–mercury amalgam, and the cathode can be either HgO (shown here) or Ag_2O as the oxidant. Button batteries are reliable and have a high output-to-mass ratio, which allows them to be used in applications such as calculators and watches, where their small size is crucial. (c) A lithium–iodine battery consists of two cells separated by a metallic nickel mesh that collects charge from the anodes. The anode is lithium metal, and the cathode is a solid complex of I_2. The electrolyte is a layer of solid LiI that allows Li^+ ions to diffuse from the cathode to the anode. Although this type of battery produces only a relatively small current, it is highly reliable and long-lived.

> The major difference between batteries and the galvanic cells is that commercial typically batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. An obvious exception is the standard car battery which used solution phase chemistry.

Leclanché Dry Cell

The dry cell, by far the most common type of battery, is used in flashlights, electronic devices such as the Walkman and Game Boy, and many other devices. Although the dry cell was patented in 1866 by the French chemist Georges Leclanché and more than 5 billion such cells are sold every year, the details of its electrode chemistry are still not completely understood. In spite of its name, the **Leclanché dry cell** is actually a "wet cell": the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch (part (a) in Figure 17.4.1). The half-reactions at the anode and the cathode can be summarized as follows:

- cathode (reduction):

$$2\,MnO_2(s) + 2\,NH_4^+(aq) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,NH_3(aq) + H_2O(l)$$

- anode (oxidation):

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$$

The Zn^{2+} ions formed by the oxidation of $Zn(s)$ at the anode react with NH_3 formed at the cathode and Cl^- ions present in solution, so the overall cell reaction is as follows:

- overall reaction:

$$2\,MnO_2(s) + 2\,NH_4Cl(aq) + Zn(s) \longrightarrow Mn_2O_3(s) + Zn(NH_3)_2Cl_2(s) + H_2O(l) \tag{17.4.1}$$

The dry cell produces about 1.55 V and is inexpensive to manufacture. It is not, however, very efficient in producing electrical energy because only the relatively small fraction of the MnO_2 that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with NH_4Cl in the electrolyte, causing the case to corrode and allowing the contents to leak out.

Close up of a hand holding one double <span class=
AA
battery" style="width: 287px; height: 215px;" width="287px" height="215px" data-cke-saved-src="/@api/deki/files/16647/battery.jpg" src="/@api/deki/files/16647/battery.jpg" data-quail-id="34">

Source: Photo courtesy of Mitchclanky2008, www.flickr.com/photos/25597837@N05/2422765479/.

The **alkaline battery** is essentially a Leclanché cell adapted to operate under alkaline, or basic, conditions. The half-reactions that occur in an alkaline battery are as follows:

- cathode (reduction)

$$2\,MnO_2(s) + H_2O(l) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,OH^-(aq)$$

- anode (oxidation):

$$Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^-$$

- overall reaction:

$$Zn(s) + 2\,MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s)$$

This battery also produces about 1.5 V, but it has a longer shelf life and more constant output voltage as the cell is discharged than the Leclanché dry cell. Although the alkaline battery is more expensive to produce than the Leclanché dry cell, the improved performance makes this battery more cost-effective.

Button Batteries

Although some of the small button batteries used to power watches, calculators, and cameras are miniature alkaline cells, most are based on a completely different chemistry. In these "button" batteries, the anode is a zinc–mercury amalgam rather than pure zinc, and the cathode uses either HgO or Ag_2O as the oxidant rather than MnO_2 in Figure 17.4.1b).

Button batteries. (Gerhard H Wrodnigg via Wikipedia)

The cathode, anode and overall reactions and cell output for these two types of button batteries are as follows (two half-reactions occur at the anode, but the overall oxidation half-reaction is shown):

- cathode (mercury battery):

$$HgO(s) + H_2O(l) + 2\,e^- \longrightarrow Hg(l) + 2\,OH^-(aq)$$

- Anode (mercury battery):

$$Zn + 2\,OH^- \longrightarrow ZnO + H_2O + 2\,e^-$$

- overall reaction (mercury battery):

$$Zn(s) + 2\,HgO(s) \longrightarrow 2\,Hg(l) + ZnO(s)$$

  with $E_{cell} = 1.35\,V$.
- cathode reaction (silver battery):

$$Ag_2O(s) + H_2O(l) + 2\,e^- \longrightarrow 2\,Ag(s) + 2\,OH^-(aq)$$

- anode (silver battery):

$$\mathrm{Zn} + 2\,\mathrm{OH}^- \longrightarrow \mathrm{ZnO} + \mathrm{H_2O} + 2\,\mathrm{e}^-$$

- Overall reaction (silver battery):

$$\mathrm{Zn(s)} + 2\,\mathrm{Ag_2O(s)} \longrightarrow 2\,\mathrm{Ag(s)} + \mathrm{ZnO(s)}$$

with $E_{cell} = 1.6\,V$.

The major advantages of the mercury and silver cells are their reliability and their high output-to-mass ratio. These factors make them ideal for applications where small size is crucial, as in cameras and hearing aids. The disadvantages are the expense and the environmental problems caused by the disposal of heavy metals, such as Hg and Ag.

Lithium–Iodine Battery

None of the batteries described above is actually "dry." They all contain small amounts of liquid water, which adds significant mass and causes potential corrosion problems. Consequently, substantial effort has been expended to develop water-free batteries. One of the few commercially successful water-free batteries is the **lithium–iodine battery**. The anode is lithium metal, and the cathode is a solid complex of I_2. Separating them is a layer of solid LiI, which acts as the electrolyte by allowing the diffusion of Li^+ ions. The electrode reactions are as follows:

- cathode (reduction):

$$I_{2(s)} + 2e^- \rightarrow 2I^-{}_{(LiI)} \tag{17.4.2}$$

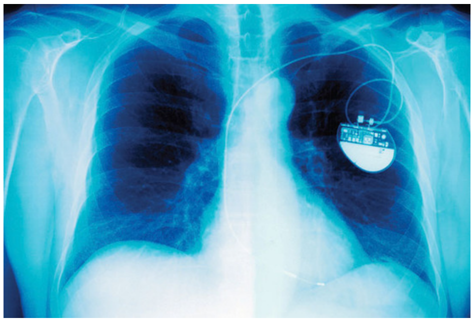
- anode (oxidation):

$$2Li_{(s)} \rightarrow 2Li^+_{(LiI)} + 2e^- \tag{17.4.3}$$

- overall:

$$2Li_{(s)} + I_{2(s)} \rightarrow 2LiI_{(s)} \tag{17.4.4}$$

with $E_{cell} = 3.5\,V$



Cardiac pacemaker: An x-ray of a patient showing the location and size of a pacemaker powered by a lithium–iodine battery.

As shown in part (c) in Figure $17.4.1$, a typical lithium–iodine battery consists of two cells separated by a nickel metal mesh that collects charge from the anode. Because of the high internal resistance caused by the solid electrolyte, only a low current can be drawn. Nonetheless, such batteries have proven to be long-lived (up to 10 yr) and reliable. They are therefore used in applications where frequent replacement is difficult or undesirable, such as in cardiac pacemakers and other medical implants and in computers for memory protection. These batteries are also used in security transmitters and smoke alarms. Other batteries based on lithium anodes and solid electrolytes are under development, using TiS_2, for example, for the cathode.

Dry cells, button batteries, and lithium–iodine batteries are disposable and cannot be recharged once they are discharged. Rechargeable batteries, in contrast, offer significant economic and environmental advantages because they can be recharged and discharged numerous times. As a result, manufacturing and disposal costs drop dramatically for a given number of hours of battery usage. Two common rechargeable batteries are the nickel–cadmium battery and the lead–acid battery, which we describe next.

Nickel–Cadmium (NiCad) Battery

The **nickel–cadmium**, or NiCad, battery is used in small electrical appliances and devices like drills, portable vacuum cleaners, and AM/FM digital tuners. It is a water-based cell with a cadmium anode and a highly oxidized nickel cathode that is usually described as the nickel(III) oxo-hydroxide, NiO(OH). As shown in Figure $17.4.2$, the design maximizes the surface area of the electrodes and minimizes the distance between them, which decreases internal resistance and makes a rather high discharge current possible.

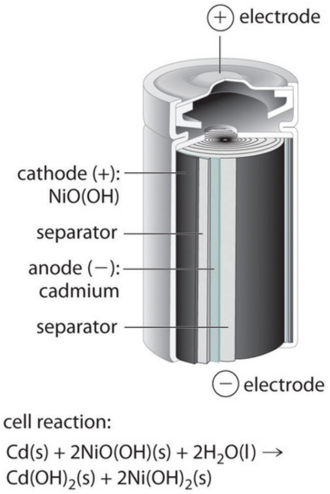


Figure 17.4.2: The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery. NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.

The electrode reactions during the discharge of a $NiCad$ battery are as follows:

- cathode (reduction):

$$2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \tag{17.4.5}$$

- anode (oxidation):

$$Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^- \tag{17.4.6}$$

- overall:

$$Cd_{(s)} + 2NiO(OH)_{(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \tag{17.4.7}$$

$$E_{cell} = 1.4 V$$

Because the products of the discharge half-reactions are solids that adhere to the electrodes [$Cd(OH)_2$ and $2Ni(OH)_2$], the overall reaction is readily reversed when the cell is recharged. Although NiCad cells are lightweight, rechargeable, and high capacity, they have certain disadvantages. For example, they tend to lose capacity quickly if not allowed to discharge fully before recharging, they do not store well for long periods when fully charged, and they present significant environmental and disposal problems because of the toxicity of cadmium.

A variation on the NiCad battery is the nickel–metal hydride battery (NiMH) used in hybrid automobiles, wireless communication devices, and mobile computing. The overall chemical equation for this type of battery is as follows:

\[NiO(OH)_{(s)} + MH \rightarrow Ni(OH)_{2(s)} + M_{(s)} \label{Eq16} \]

The NiMH battery has a 30%–40% improvement in capacity over the NiCad battery; it is more environmentally friendly so storage, transportation, and disposal are not subject to environmental control; and it is not as sensitive to recharging memory. It is, however, subject to a 50% greater self-discharge rate, a limited service life, and higher maintenance, and it is more expensive than the NiCad battery.

> Directive 2006/66/EC of the European Union prohibits the placing on the market of portable batteries that contain more than 0.002% of cadmium by weight. The aim of this directive was to improve "the environmental performance of batteries and accumulators"

Lead–Acid (Lead Storage) Battery

The **lead–acid battery** is used to provide the starting power in virtually every automobile and marine engine on the market. Marine and car batteries typically consist of multiple cells connected in series. The total voltage generated by the battery is the potential per cell ($E°_{cell}$) times the number of cells.

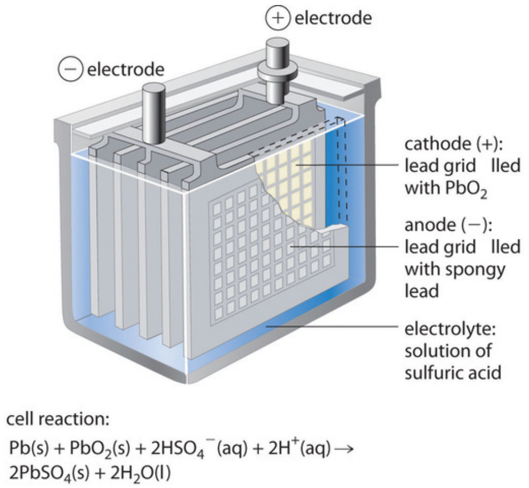


Figure 17.4.3: One Cell of a Lead–Acid Battery. The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulfuric acid. The value of E° for such a cell is about 2 V. Connecting three such cells in series produces a 6 V battery, whereas a typical 12 V car battery contains six cells in series. When treated properly, this type of high-capacity battery can be discharged and recharged many times over.

As shown in Figure $17.4.3$, the anode of each cell in a lead storage battery is a plate or grid of spongy lead metal, and the cathode is a similar grid containing powdered lead dioxide (PbO_2). The electrolyte is usually an approximately 37% solution (by mass) of sulfuric acid in water, with a density of 1.28 g/mL (about 4.5 M H_2SO_4). Because the redox active species are solids, there is no need to separate the electrodes. The electrode reactions in each cell during discharge are as follows:

- cathode (reduction):

\[PbO_{2(s)} + HSO^−_{4(aq)} + 3H^+_{(aq)} + 2e^− \rightarrow PbSO_{4(s)} + 2H_2O_{(l)} \label{Eq17} \]

with $E^\circ_{cathode} = 1.685\ V$

- anode (oxidation):

$$Pb_{(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^- \tag{17.4.8}$$

with $E^\circ_{anode} = -0.356\ V$

- overall:

$$Pb_{(s)} + PbO_{2(s)} + 2HSO^-_{4(aq)} + 2H^+_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)} \tag{17.4.9}$$

and $E^\circ_{cell} = 2.041\ V$

As the cell is discharged, a powder of $PbSO_4$ forms on the electrodes. Moreover, sulfuric acid is consumed and water is produced, decreasing the density of the electrolyte and providing a convenient way of monitoring the status of a battery by simply measuring the density of the electrolyte. This is often done with the use of a hydrometer.

A hydrometer can be used to test the specific gravity of each cell as a measure of its state of charge (www.youtube.com/watch?v=SRcOqfL6GqQ).

When an external voltage in excess of 2.04 V per cell is applied to a lead–acid battery, the electrode reactions reverse, and $PbSO_4$ is converted back to metallic lead and PbO_2. If the battery is recharged too vigorously, however, electrolysis of water can occur:

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{17.4.10}$$

This results in the evolution of potentially explosive hydrogen gas. The gas bubbles formed in this way can dislodge some of the $PbSO_4$ or PbO_2 particles from the grids, allowing them to fall to the bottom of the cell, where they can build up and cause an internal short circuit. Thus the recharging process must be carefully monitored to optimize the life of the battery. With proper care, however, a lead–acid battery can be discharged and recharged thousands of times. In automobiles, the alternator supplies the electric current that causes the discharge reaction to reverse.

Fuel Cells

A fuel cell is a galvanic cell that requires a constant external supply of reactants because the products of the reaction are continuously removed. Unlike a battery, it does not store chemical or electrical energy; a fuel cell allows electrical energy to be extracted directly from a chemical reaction. In principle, this should be a more efficient process than, for example, burning the fuel to drive an internal combustion engine that turns a generator, which is typically less than 40% efficient, and in fact, the efficiency of a fuel cell is generally between 40% and 60%. Unfortunately, significant cost and reliability problems have hindered the wide-scale adoption of fuel cells. In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles.

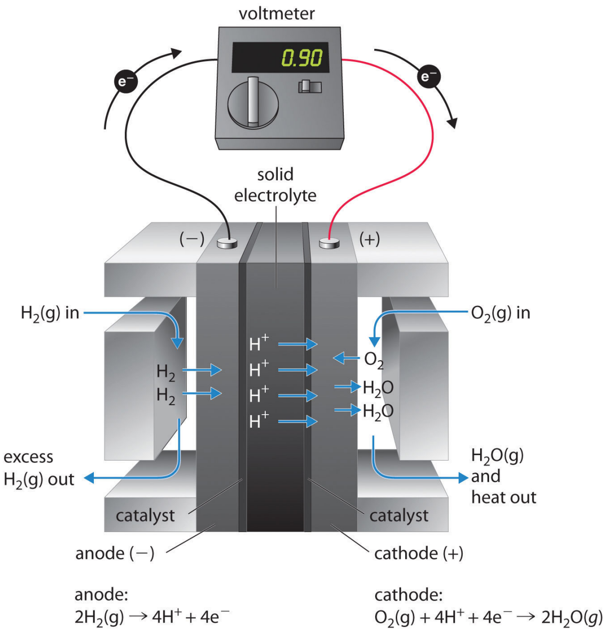


Figure 17.4.4: A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction. Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte allows the protons to diffuse from the anode to the cathode. Although fuel cells are an essentially pollution-free means of obtaining electrical energy, their expense and technological complexity have thus far limited their applications.

These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of H_2(g) and O_2(g), as illustrated in Figure 17.4.4. The electrode reactions are as follows:

- cathode (reduction):

$$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O_{(g)} \tag{17.4.11}$$

- anode (oxidation):

$$2H_{2(g)} \rightarrow 4H^+ + 4e^- \tag{17.4.12}$$

- overall:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{17.4.13}$$

The overall reaction represents an essentially pollution-free conversion of hydrogen and oxygen to water, which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23 V under standard conditions, in practice the device achieves only about 0.9 V. One of the major barriers to achieving greater efficiency is the fact that the four-electron reduction of $O_2(g)$ at the cathode is intrinsically rather slow, which limits current that can be achieved. All major automobile manufacturers have major research programs involving fuel cells: one of the most important goals is the development of a better catalyst for the reduction of $O_2(g)$.

Summary

Commercial batteries are galvanic cells that use solids or pastes as reactants to maximize the electrical output per unit mass. A battery is a contained unit that produces electricity, whereas a fuel cell is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. One type of battery is the Leclanché dry cell, which contains an electrolyte in an acidic water-based paste. This battery is called an alkaline battery when adapted to operate under alkaline conditions. Button batteries have a high output-to-mass ratio; lithium–iodine batteries consist of a solid electrolyte; the nickel–cadmium (NiCad) battery is rechargeable; and the lead–acid battery, which is also rechargeable, does not require the electrodes to be in separate compartments. A fuel cell requires an external supply of reactants as the products of the reaction are continuously removed. In a fuel cell, energy is not stored; electrical energy is provided by a chemical reaction.

17.5: Corrosion and Its Prevention

Learning Objectives

- To understand the process of corrosion.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a patina. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion. We also examine the chemical basis for some common methods for preventing corrosion and treating corroded metals.

> *Corrosion is a REDOX process.*

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth's moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminum cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both.

In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($\mathrm{Fe_2O_3 \cdot xH_2O}$), commonly known as rust, that does not provide a tight protective film (Figure $17.5.1$). Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil will not rust because of the absence of water even if the solvent is saturated with oxygen.

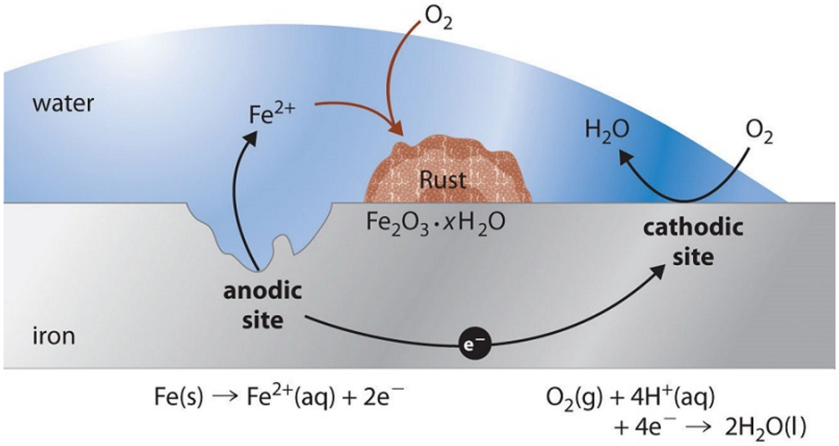


Figure 17.5.1: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to Fe^{2+}(aq) at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust ($Fe_2O_3 \cdot xH_2O$) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen. (CC BY-NC-SA; anonymous)

In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to Fe^{2+}; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

- at cathode:

$$\mathrm{O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)}$$

with $E^o_{SRP} = 1.23\ V$.

- at anode:

$$\mathrm{Fe(s)} \longrightarrow \mathrm{Fe^{2\,+}(aq)} + 2\,\mathrm{e^-}$$

  with $E^o_{SRP} = -0.45\ V$.
- overall:

$$2\,\mathrm{Fe(s)} + \mathrm{O_2(g)} + 4\,\mathrm{H^+(aq)} \longrightarrow 2\,\mathrm{Fe^{2\,+}(aq)} + 2\,\mathrm{H_2O(l)} \tag{17.5.1}$$

  with $E^o_{cell} = 1.68\ V$.

The $\mathrm{Fe^{2\,+}}$ ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing $\mathrm{Fe^{3\,+}}$, as represented in the following equation:

$$4\,\mathrm{Fe^{2\,+}(aq)} + \mathrm{O_2(g)} + (2\ + 4\,\mathrm{x})\mathrm{H_2O} \rightarrow 2\,\mathrm{Fe_2O_3} \cdot \mathrm{xH_2O} + 4\,\mathrm{H^+(aq)} \tag{17.5.2}$$

The sign and magnitude of E^o_{cell} for the corrosion process (Equation 17.5.1) indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^+). Under neutral conditions, the driving force is somewhat less but still appreciable (E = 1.25 V at pH 7.0). Normally, the reaction of atmospheric CO_2 with water to form H^+ and HCO_3^- provides a low enough pH to enhance the reaction rate, as does acid rain. Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car's metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure (Figure 17.5.2).

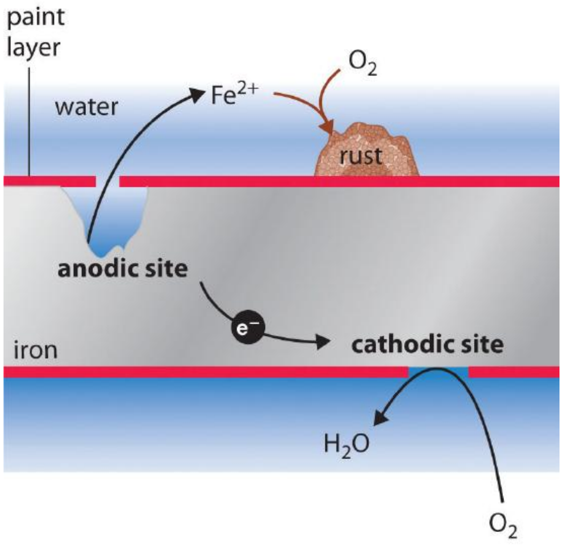


Figure 17.5.2: Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to Fe^{2+}(aq) at the less exposed site (the anode). Rust is formed when Fe^{2+}(aq) diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form under a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.

Prophylactic Protection

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process. With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the "tin cans" that hold soups and other foods are actually consist of steel container that is coated with a thin layer of tin. While neither chromium nor tin metals are intrinsically resistant to corrosion, they both form protective oxide coatings that hinder access of oxygen and water to the underlying steel (iron alloy).

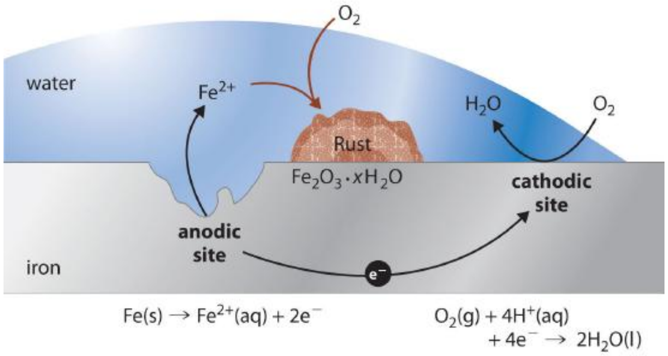


Figure 17.5.3: Galvanic Corrosion. If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can result in a dramatic increase in the rate at which iron is oxidized at the anode. Galvanic corrosion is likely to occur whenever two dissimilar metals are connected directly, allowing electrons to be transferred from one to the other.

As with a protective paint, scratching a protective metal coating will allow corrosion to occur. In this case, however, the presence of the second metal can actually increase the rate of corrosion. The values of the standard electrode potentials for Sn^{2+} (E° = −0.14 V) and Fe^{2+} (E° = −0.45 V) in Table P2 show that Fe is more easily oxidized than Sn. As a result, the more corrosion-resistant metal (in this case, tin) accelerates the corrosion of iron by acting as the cathode and providing a large surface area for the reduction of oxygen (Figure 17.5.3). This process is seen in some older homes where copper and iron pipes have been directly connected to each other. The less easily oxidized copper acts as the cathode, causing iron to dissolve rapidly near the connection and occasionally resulting in a catastrophic plumbing failure.

Cathodic Protection

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called cathodic protection, a more reactive metal such as Zn (E° = −0.76 V for $\mathrm{Zn}^{2+} + 2\,\mathrm{e}^- \longrightarrow \mathrm{Zn}$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:

$$\underbrace{O_{2(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}}_{\text{reduction at cathode}} \tag{17.5.3}$$

$$\underbrace{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}_{\text{oxidation at anode}} \tag{17.5.4}$$

$$\underbrace{2Zn_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Zn^{2+}_{(aq)} + 2H_2O_{(l)}}_{\text{overall}} \tag{17.5.5}$$

The more reactive metal reacts with oxygen and will eventually dissolve, “sacrificing” itself to protect the iron object. Cathodic protection is the principle underlying galvanized steel, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans.

Crystalline surface of a hot-dip galvanized steel surface. This served both as prophylactic protection (protecting the underlying steel from the oxygen in the air) and cathodic protection (once exposed, the zinc will oxidize before the underlying steel).

In a similar strategy, **sacrificial electrodes** using magnesium, for example, are used to protect underground tanks or pipes (Figure 17.5.4). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

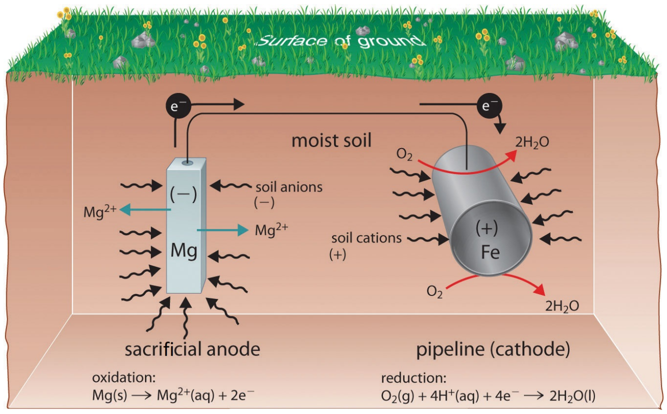


Figure 17.5.4: The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium (E° = −2.37 V) is much more easily oxidized than iron (E° = −0.45 V), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to Mg^{2+} at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as H^+ or NH_4^+, diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.

✓ Example 17.5.1

Suppose an old wooden sailboat, held together with iron screws, has a bronze propeller (recall that bronze is an alloy of copper containing about 7%–10% tin).

a. If the boat is immersed in seawater, what corrosion reaction will occur? What is $E^{o\circ}{}_{cell}$?
b. How could you prevent this corrosion from occurring?

Given: identity of metals

Asked for: corrosion reaction, $E^{o\circ}{}_{cell}$, and preventive measures

Strategy:

A. Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate $E^{o\circ}{}_{cell}$.
B. Based on the relative redox activity of various substances, suggest possible preventive measures.

Solution

a. **A** According to Table P2, both copper and tin are less active metals than iron (i.e., they have higher positive values of $E^{o\circ}{}_{cell}$ than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which O_2 is reduced, and the iron screws will act as anodes at which iron dissolves:

$$\begin{array}{lll}\text{cathode:} & O_2(s) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) & E^\circ_{\text{cathode}} = 1.23\text{ V} \\ \text{anode:} & Fe(s) \rightarrow Fe^{2+} + 2e^- & E^\circ_{\text{anode}} = -0.45\text{ V} \\ \text{overall:} & 2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l) & E^\circ_{\text{overall}} = 1.68\text{ V}\end{array}$$

Over time, the iron screws will dissolve, and the boat will fall apart.

b. **B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 17.5.5).

Zinc sacrificial anode (rounded object screwed to underside of hull) used to prevent corrosion on the screw in a boat via cathodic protection. Image by Rémi Kaupp and used with permission.

Exercise 17.5.1

Suppose the water pipes leading into your house are made of lead, while the rest of the plumbing in your house is iron. To eliminate the possibility of lead poisoning, you call a plumber to replace the lead pipes. He quotes you a very low price if he can use up his existing supply of copper pipe to do the job.

a. Do you accept his proposal?
b. What else should you have the plumber do while at your home?

Answer a

Not unless you plan to sell the house very soon because the $\mathrm{Cu/Fe}$ pipe joints will lead to rapid corrosion.

Answer b

Any existing $\mathrm{Pb/Fe}$ joints should be examined carefully for corrosion of the iron pipes due to the $\mathrm{Pb–Fe}$ junction; the less active Pb will have served as the cathode for the reduction of $\mathrm{O_2}$, promoting oxidation of the more active Fe nearby.

Summary

Corrosion is a galvanic process that can be prevented using cathodic protection. The deterioration of metals through oxidation is a galvanic process called corrosion. Protective coatings consist of a second metal that is more difficult to oxidize than the metal being protected. Alternatively, a more easily oxidized metal can be applied to a metal surface, thus providing cathodic protection of the surface. A thin layer of zinc protects galvanized steel. Sacrificial electrodes can also be attached to an object to protect it.

17.6: Electrometallurgy

23.4: Electrometallurgy

17.7: A Deeper Look: Electrolysis of Water and Aqueous Solutions

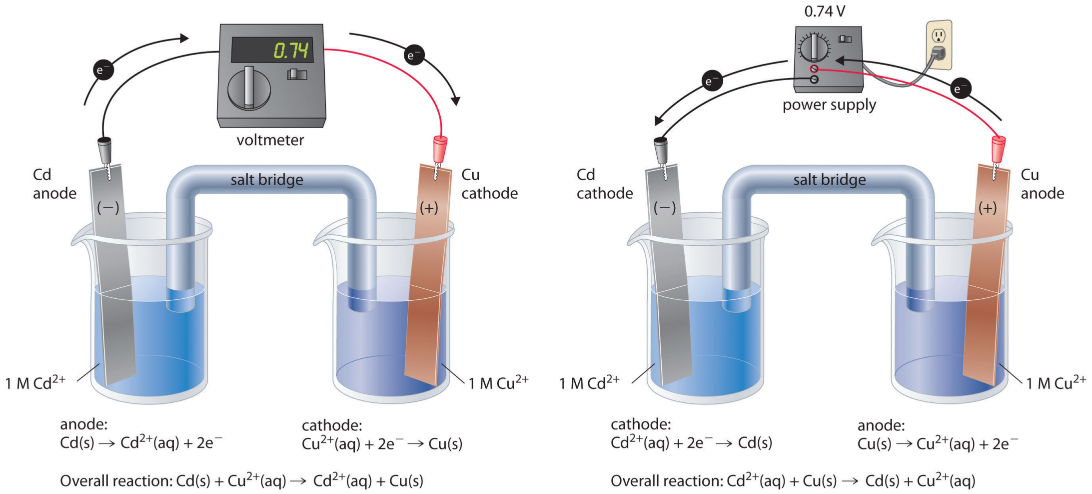
Learning Objectives

- To understand electrolysis and describe it quantitatively.

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called **electrolysis**, occurs: an external voltage is applied to drive a nonspontaneous reaction. In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

Electrolytic Cells

If we construct an electrochemical cell in which one electrode is copper metal immersed in a 1 M Cu^{2+} solution and the other electrode is cadmium metal immersed in a $1\ M\ Cd^{2+}$ solution and then close the circuit, the potential difference between the two compartments will be 0.74 V. The cadmium electrode will begin to dissolve (Cd is oxidized to Cd^{2+}) and is the anode, while metallic copper will be deposited on the copper electrode (Cu^{2+} is reduced to Cu), which is the cathode (Figure $17.7.1a$).



(a) Galvanic cell **(b) Electrolytic cell**

Figure 17.7.1: An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell. (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) at the anode, and Cu^{2+}(aq) is spontaneously reduced to Cu(s) at the cathode. The potential of the galvanic cell is 0.74 V. (b) Applying an external potential greater than 0.74 V in the reverse direction forces electrons to flow from the Cu electrode [which is now the anode, at which metallic Cu(s) is oxidized to Cu^{2+}(aq)] and into the Cd electrode [which is now the cathode, at which Cd^{2+}(aq) is reduced to Cd(s)]. The anode in an electrolytic cell is positive because electrons are flowing from it, whereas the cathode is negative because electrons are flowing into it. (CC BY-SA-NC; anonymous)

The overall reaction is as follows:

$$\mathrm{Cd(s) + Cu^{2\,+}(aq) \rightarrow Cd^{2\,+}(aq) + Cu(s)}$$

with $E^\circ{}_{cell} = 0.74\ V$

This reaction is thermodynamically spontaneous as written ($\Delta G^o < 0$):

$$\begin{aligned}\Delta G^\circ &= -nFE^\circ_{\text{cell}} \\ &= -(2\text{ mol e}^-)[96,485\text{ J/(V}\cdot\text{mol)}](0.74\text{ V}) \\ &= -140\text{ kJ (per mole Cd)}\end{aligned}$$

In this direction, the system is acting as a galvanic cell.

> *In an electrolytic cell, an external voltage is applied to drive a nonspontaneous reaction.*

The reverse reaction, the reduction of Cd^{2+} by Cu, is thermodynamically nonspontaneous and will occur only with an input of 140 kJ. We can force the reaction to proceed in the reverse direction by applying an electrical potential greater than 0.74 V from an external power supply. The applied voltage forces electrons through the circuit in the reverse direction, converting a galvanic cell to an electrolytic cell. Thus the copper electrode is now the anode (Cu is oxidized), and the cadmium electrode is now the cathode (Cd^{2+} is reduced) (Figure $17.7.1b$). The signs of the cathode and the anode have switched to reflect the flow of electrons in the circuit. The half-reactions that occur at the cathode and the anode are as follows:

- half-reaction at the cathode:

$$\mathrm{Cd^{2\,+}(aq) + 2\,e^- \rightarrow Cd(s)} \tag{17.7.1}$$

with $E^\circ_{cathode} = -0.40\,V$

- half-reaction at the anode:

$$\mathrm{Cu(s) \rightarrow Cu^{2\,+}(aq) + 2\,e^-} \tag{17.7.2}$$

with $E^\circ_{anode} = 0.34\,V$

- Overall Reaction:

$$\mathrm{Cd^{2\,+}(aq) + Cu(s) \rightarrow Cd(s) + Cu^{2\,+}(aq)} \tag{17.7.3}$$

with $E^\circ_{cell} = -0.74\,V$

Because $E^\circ_{cell} < 0$, the overall reaction—the reduction of Cd^{2+} by Cu—clearly **cannot** occur spontaneously and proceeds only when sufficient electrical energy is applied. The differences between galvanic and electrolytic cells are summarized in Table $17.7.1$.

Table 17.7.1: Comparison of Galvanic and Electrolytic Cells

Property	Galvanic Cell	Electrolytic Cell
ΔG	< 0	> 0
E_{cell}	> 0	< 0
Electrode Process		
anode	oxidation	oxidation
cathode	reduction	reduction
Sign of Electrode		
anode	−	+
cathode	+	−

Electrolytic Reactions

At sufficiently high temperatures, ionic solids melt to form liquids that conduct electricity extremely well due to the high concentrations of ions. If two inert electrodes are inserted into molten NaCl, for example, and an electrical potential is applied, $\mathrm{Cl^-}$ is oxidized at the anode, and $\mathrm{Na^+}$ is reduced at the cathode. The overall reaction is as follows:

$$\mathrm{2\,NaCl(l) \rightarrow 2\,Na(l) + Cl_2(g)} \tag{17.7.4}$$

This is the reverse of the formation of NaCl from its elements. The product of the reduction reaction is liquid sodium because the melting point of sodium metal is 97.8°C, well below that of NaCl (801°C). Approximately 20,000 tons of sodium metal are produced commercially in the United States each year by the electrolysis of molten NaCl in a Downs cell (Figure $17.7.2$). In this specialized cell, $\mathrm{CaCl_2}$ (melting point = 772°C) is first added to the NaCl to lower the melting point of the mixture to about 600°C, thereby lowering operating costs.

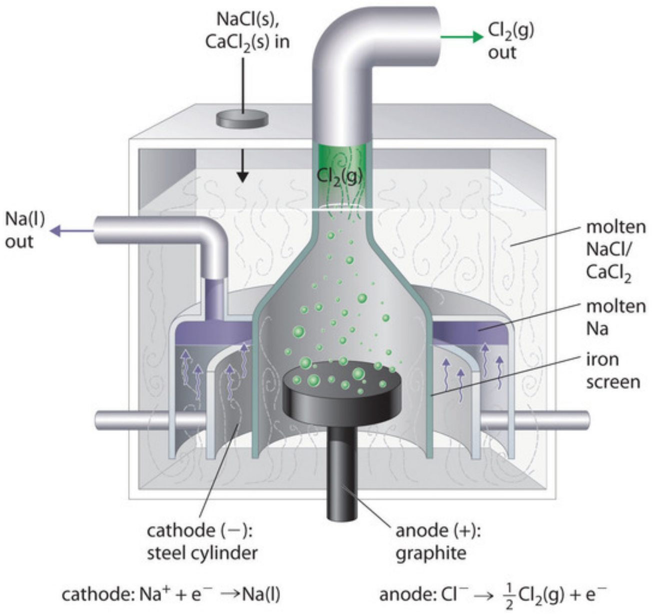


Figure 17.7.2: A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and CaCl$_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium floats to the top of the melt and is collected in concentric capped iron cylinders surrounding the cathode. Gaseous chlorine collects in the inverted cone over the anode. An iron screen separating the cathode and anode compartments ensures that the molten sodium and gaseous chlorine do not come into contact. (CC BY-SA-NC; anonymous)

Similarly, in the Hall–Heroult process used to produce aluminum commercially, a molten mixture of about 5% aluminum oxide (Al_2O_3; melting point = 2054°C) and 95% cryolite (Na_3AlF_6; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and CO_2 gas at the carbon anode. The overall reaction is as follows:

$$2\,Al_2O_3(l) + 3\,C(s) \longrightarrow 4\,Al(l) + 3\,CO_2(g) \tag{17.7.5}$$

Oxide ions react with oxidized carbon at the anode, producing CO_2(g).

There are two important points to make about these two commercial processes and about the electrolysis of molten salts in general.

1. The electrode potentials for molten salts are likely to be very different from the standard cell potentials listed in Table P2, which are compiled for the reduction of the hydrated ions in aqueous solutions under standard conditions.
2. Using a mixed salt system means there is a possibility of competition between different electrolytic reactions. When a mixture of NaCl and $CaCl_2$ is electrolyzed, Cl^- is oxidized because it is the only anion present, but either Na^+ or Ca^{2+} can be reduced. Conversely, in the Hall–Heroult process, only one cation is present that can be reduced (Al^{3+}), but there are three species that can be oxidized: C, O^{2-}, and F^-.

In the Hall–Heroult process, C is oxidized instead of O^{2-} or F^- because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either O_2 or F_2. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/$CaCl_2$ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca (χ = 0.93 versus 1.00, respectively), making Na easier to oxidize and, conversely, Na^+ more difficult to reduce. In fact, the reduction of Na^+ to Na is the observed reaction. In cases where the electronegativities of two species are similar, other factors, such as the formation of complex ions, become important and may determine the outcome.

✓ Example 17.7.1

If a molten mixture of $MgCl_2$ and KBr is electrolyzed, what products will form at the cathode and the anode, respectively?

Given: identity of salts

Asked for: electrolysis products

Strategy:

A. List all the possible reduction and oxidation products. Based on the electronegativity values shown in Figure 7.5, determine which species will be reduced and which species will be oxidized.
B. Identify the products that will form at each electrode.

Solution

A The possible reduction products are Mg and K, and the possible oxidation products are Cl_2 and Br_2. Because Mg is more electronegative than K (χ = 1.31 versus 0.82), it is likely that Mg will be reduced rather than K. Because Cl is more electronegative than Br (3.16 versus 2.96), Cl_2 is a stronger oxidant than Br_2.

B Electrolysis will therefore produce Br_2 at the anode and Mg at the cathode.

? Exercise 17.7.1

Predict the products if a molten mixture of $AlBr_3$ and LiF is electrolyzed.

Answer

Br_2 and Al

Electrolysis can also be used to drive the thermodynamically nonspontaneous decomposition of water into its constituent elements: H_2 and O_2. However, because pure water is a very poor electrical conductor, a small amount of an ionic solute (such as H_2SO_4 or Na_2SO_4) must first be added to increase its electrical conductivity. Inserting inert electrodes into the solution and applying a voltage between them will result in the rapid evolution of bubbles of H_2 and O_2 (Figure 17.7.3).

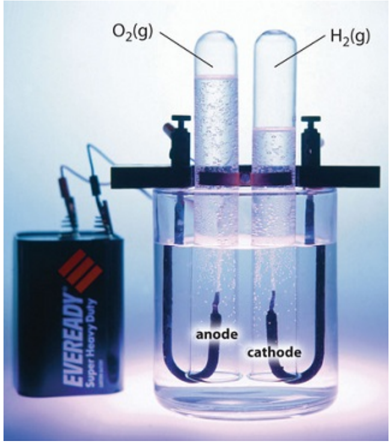


Figure 17.7.3: The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode. (CC BY-SA-NC; anonymous)

The reactions that occur are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ_{cathode} = 0V \tag{17.7.6}$$

- anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \qquad E^\circ_{anode} = 1.23\ V \tag{17.7.7}$$

- overall:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad E^\circ_{cell} = -1.23\ V \tag{17.7.8}$$

For a system that contains an electrolyte such as Na_2SO_4, which has a negligible effect on the ionization equilibrium of liquid water, the pH of the solution will be 7.00 and $[H^+] = [OH^-] = 1.0 \times 10^{-7}$. Assuming that $P_{O_2} = P_{H_2} = 1$ atm, we can use the standard potentials to calculate E for the overall reaction:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\text{ V}}{n}\right)\log(P_{O_2}P^2_{H_2}) \tag{17.7.9}$$

$$= -1.23\text{ V} - \left(\frac{0.0591\text{ V}}{4}\right)\log(1) = -1.23\text{ V} \tag{17.7.10}$$

Thus E_{cell} is −1.23 V, which is the value of $E°_{cell}$ if the reaction is carried out in the presence of 1 M H^+ rather than at pH 7.0.

In practice, a voltage about 0.4–0.6 V greater than the calculated value is needed to electrolyze water. This added voltage, called an **overvoltage**, represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface. Overvoltages are needed in all electrolytic processes, which explain why, for example, approximately 14 V must be applied to recharge the 12 V battery in your car.

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation. The p-block metals and most of the transition metals are in this category, but metals in high oxidation states, which form oxoanions, cannot be reduced to the metal by simple electrolysis. Active metals, such as aluminum and those of groups 1 and 2, react so readily with water that they can be prepared only by the electrolysis of molten salts. Similarly, any nonmetallic element that does not readily oxidize water to O_2 can be prepared by the electrolytic oxidation of an aqueous solution that contains an appropriate anion. In practice, among the nonmetals, only F_2 cannot be prepared using this method. Oxoanions of nonmetals in their highest oxidation states, such as NO_3^-, SO_4^{2-}, PO_4^{3-}, are usually difficult to reduce electrochemically and usually behave like spectator ions that remain in solution during electrolysis.

> *In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation.*

Electroplating

In a process called **electroplating**, a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis. Electroplating is used to enhance the appearance of metal objects and protect them from corrosion. Examples of electroplating include the chromium layer found on many bathroom fixtures or (in earlier days) on the bumpers and hubcaps of cars, as well as the thin layer of precious metal that coats silver-plated dinnerware or jewelry. In all cases, the basic concept is the same. A schematic view of an apparatus for electroplating silverware and a photograph of a commercial electroplating cell are shown in Figure 17.7.4

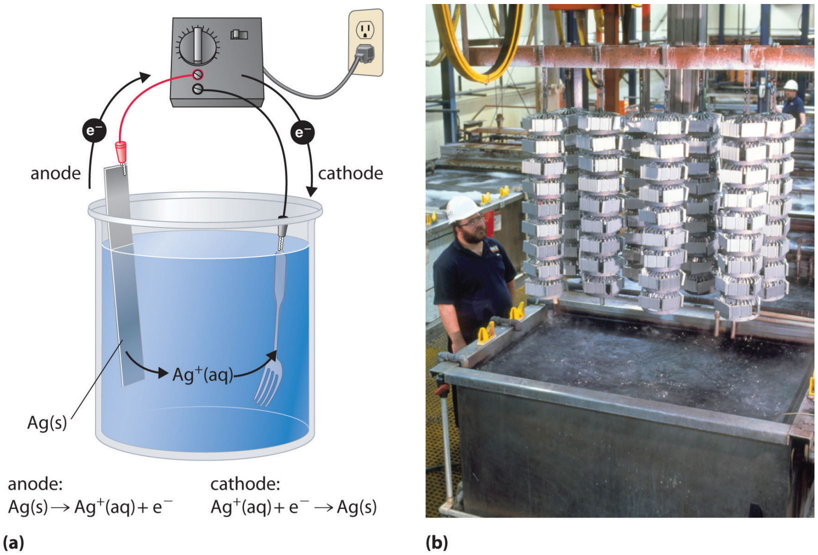


Figure 17.7.3: Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually consists of the metal that is being deposited (in this case, silver) that maintains the solution concentration as it dissolves. (b) In this commercial electroplating apparatus, a large number of objects can be plated simultaneously by lowering the rack into the Ag^+ solution and applying the correct potential. (CC BY-SA-NC; anonymous)

The half-reactions in electroplating a fork, for example, with silver are as follows:

- cathode (fork):

$$\mathrm{Ag^+(aq) + e^- \longrightarrow Ag(s)} \qquad E^\circ{}_{cathode} = 0.80V$$

- anode (silver bar):

$$\mathrm{Ag(s) \longrightarrow Ag^+(aq) + e^-} \qquad E^\circ{}_{anode} = 0.80V$$

The overall reaction is the transfer of silver metal from one electrode (a silver bar acting as the anode) to another (a fork acting as the cathode). Because $E^o_{cell} = 0\,V$, it takes only a small applied voltage to drive the electroplating process. In practice, various other substances may be added to the plating solution to control its electrical conductivity and regulate the concentration of free metal ions, thus ensuring a smooth, even coating.

Quantitative Considerations

If we know the stoichiometry of an electrolysis reaction, the amount of current passed, and the length of time, we can calculate the amount of material consumed or produced in a reaction. Conversely, we can use stoichiometry to determine the combination of current and time needed to produce a given amount of material.

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the stoichiometry of the reaction and the amount of charge that is transferred. For example, in the reaction

$$\mathrm{Ag^+(aq) + e^- \rightarrow Ag(s)}$$

1 mol of electrons reduces 1 mol of $\mathrm{Ag^+}$ to Ag metal. In contrast, in the reaction

$$\mathrm{Cu^{2\,+}(aq) + 2\,e^- \rightarrow Cu(s)}$$

1 mol of electrons reduces only 0.5 mol of $\mathrm{Cu^{2\,+}}$ to Cu metal. Recall that the charge on 1 mol of electrons is 1 faraday (1 F), which is equal to 96,485 C. We can therefore calculate the number of moles of electrons transferred when a known current is passed through a cell for a given period of time. The total charge (q in coulombs) transferred is the product of the current (I in amperes) and the time (t, in seconds):

$$q = I \times t \tag{17.7.11}$$

The stoichiometry of the reaction and the total charge transferred enable us to calculate the amount of product formed during an electrolysis reaction or the amount of metal deposited in an electroplating process.

For example, if a current of 0.60 A passes through an aqueous solution of $\mathrm{CuSO_4}$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$\begin{aligned} q &= \mathrm{(0.60\ A)(6.0\ min)(60\ s/min)} \\ &= \mathrm{220\ A \cdot s} \\ &= \mathrm{220\ C} \end{aligned}$$

The number of moles of electrons transferred to $\mathrm{Cu^{2\,+}}$ is therefore

$$\begin{aligned} \mathrm{moles\ e^-} &= \mathrm{\frac{220\ C}{96{,}485\ C/mol}} \\ &= \mathrm{2.3 \times 10^{-3}\ mol\ e^-} \end{aligned}$$

Because two electrons are required to reduce a single Cu^{2+} ion, the total number of moles of Cu produced is half the number of moles of electrons transferred, or 1.2×10^{-3} mol. This corresponds to 76 mg of Cu. In commercial electrorefining processes, much higher currents (greater than or equal to 50,000 A) are used, corresponding to approximately 0.5 F/s, and reaction times are on the order of 3–4 weeks.

✓ Example 17.7.2

A silver-plated spoon typically contains about 2.00 g of Ag. If 12.0 h are required to achieve the desired thickness of the Ag coating, what is the average current per spoon that must flow during the electroplating process, assuming an efficiency of 100%?

Given: mass of metal, time, and efficiency

Asked for: current required

Strategy:

A. Calculate the number of moles of metal corresponding to the given mass transferred.
B. Write the reaction and determine the number of moles of electrons required for the electroplating process.
C. Use the definition of the faraday to calculate the number of coulombs required. Then convert coulombs to current in amperes.

Solution

A We must first determine the number of moles of Ag corresponding to 2.00 g of Ag:

$$\text{moles Ag} = \frac{2.00\text{ g}}{107.868\text{ g/mol}} = 1.85 \times 10^{-2}\text{ mol Ag}$$

B The reduction reaction is $Ag^+(aq) + e^- \rightarrow Ag(s)$, so 1 mol of electrons produces 1 mol of silver.

C Using the definition of the faraday,

$$\text{coulombs} = (1.85 \times 10^{-2}\text{mol e}^-)(96{,}485\text{ C/mol e}^-) = 1.78 \times 10^3\text{ C / mole}$$

The current in amperes needed to deliver this amount of charge in 12.0 h is therefore

$$\begin{aligned}\text{amperes} &= \frac{1.78 \times 10^3\text{ C}}{(12.0\text{ h})(60\text{ min/h})(60\text{ s/min})} \\ &= 4.12 \times 10^{-2}\text{ C/s} = 4.12 \times 10^{-2}\text{ A}\end{aligned}$$

Because the electroplating process is usually much less than 100% efficient (typical values are closer to 30%), the actual current necessary is greater than 0.1 A.

? Exercise 17.7.2

A typical aluminum soft-drink can weighs about 29 g. How much time is needed to produce this amount of Al(s) in the Hall–Heroult process, using a current of 15 A to reduce a molten Al_2O_3/Na_3AlF_6 mixture?

Answer

5.8 h

Electroplating: Electroplating(opens in new window) [youtu.be]

Summary

In electrolysis, an external voltage is applied to drive a **nonspontaneous** reaction. The quantity of material oxidized or reduced can be calculated from the stoichiometry of the reaction and the amount of charge transferred. Relationship of charge, current and time:

$$q = I \times t$$

In electrolysis, an external voltage is applied to drive a nonspontaneous reaction. Electrolysis can also be used to produce H_2 and O_2 from water. In practice, an additional voltage, called an overvoltage, must be applied to overcome factors such as a large activation energy and a junction potential. Electroplating is the process by which a second metal is deposited on a metal surface, thereby enhancing an object's appearance or providing protection from corrosion. The amount of material consumed or produced in a reaction can be calculated from the stoichiometry of an electrolysis reaction, the amount of current passed, and the duration of the electrolytic reaction.

SECTION OVERVIEW

Unit 5: Rates of Chemical and Physical Processes

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

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CHAPTER OVERVIEW

18: Chemical Kinetics

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

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This chapter will present a quantitative description of when the chemical composition of a system is *not* constant with time. Chemical kinetics is the study of reaction rates, the changes in the concentrations of reactants and products with time. With a discussion of chemical kinetics, the reaction rates or the changes in the concentrations of reactants and products with time are studied. The techniques you are about to learn will enable you to describe the speed of many such changes and predict how the composition of each system will change in response to changing conditions. As you learn about the factors that affect reaction rates, the methods chemists use for reporting and calculating those rates, and the clues that reaction rates provide about events at the molecular level.

18.1: Rates of Chemical Reactions

Learning Objectives

- To determine the reaction rate of a reaction.

Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the change in the concentration per unit time.

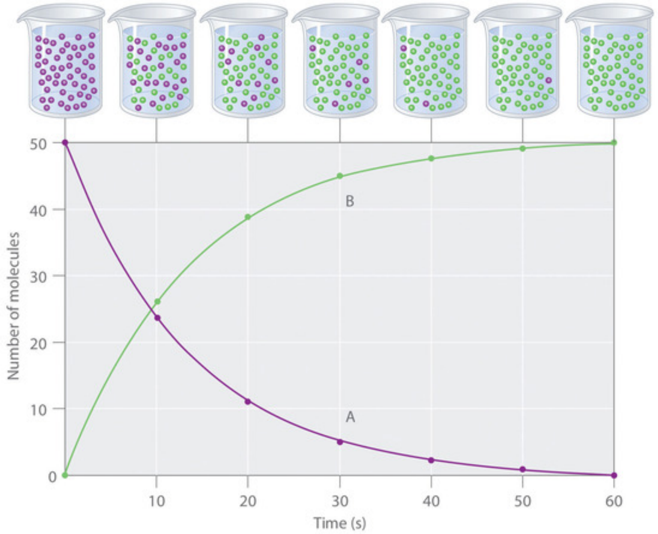


Figure 18.1.1: The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

The progress of a simple reaction (A → B) is shown in Figure 18.1.1; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure 18.1.1. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{18.1.1}$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means “change in.” Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of Δ[A]/Δt to convert that expression to a positive number. The reaction rate calculated for the reaction A → B using Equation 18.1.1 is different for each interval (this is not true for every reaction, as shown below). A greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, meaning that the reaction rate is greatest at first.

> *Reaction rates generally decrease with time as reactant concentrations decrease.*

A Video Discussing Average Reaction Rates. Video Link: Introduction to Chemical Reaction Kinetics(opens in new window) [youtu.be] (opens in new window)

Determining the Reaction Rate of Hydrolysis of Aspirin

We can use Equation 18.1.1 to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world (more than 25,000,000 kg are produced annually worldwide). Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid, as shown in Figure 18.1.2.

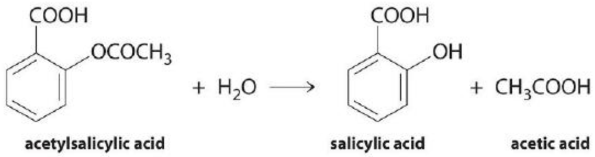


Figure 18.1.2: Hydrolysis of Aspirin reaction.

Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table 18.1.1 and are shown in the graph in Figure 18.1.3.

Table 18.1.1: Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55 × 10^{-3}	0
2.0	5.51 × 10^{-3}	0.040 × 10^{-3}
5.0	5.45 × 10^{-3}	0.10 × 10^{-3}
10	5.35 × 10^{-3}	0.20 × 10^{-3}
20	5.15 × 10^{-3}	0.40 × 10^{-3}
30	4.96 × 10^{-3}	0.59 × 10^{-3}
40	4.78 × 10^{-3}	0.77 × 10^{-3}
50	4.61 × 10^{-3}	0.94 × 10^{-3}
100	3.83 × 10^{-3}	1.72 × 10^{-3}
200	2.64 × 10^{-3}	2.91 × 10^{-3}
300	1.82 × 10^{-3}	3.73 × 10^{-3}

*The reaction at pH 7.0 is very slow. It is much faster under acidic conditions, such as those found in the stomach.

The data in Table 18.1.1 were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

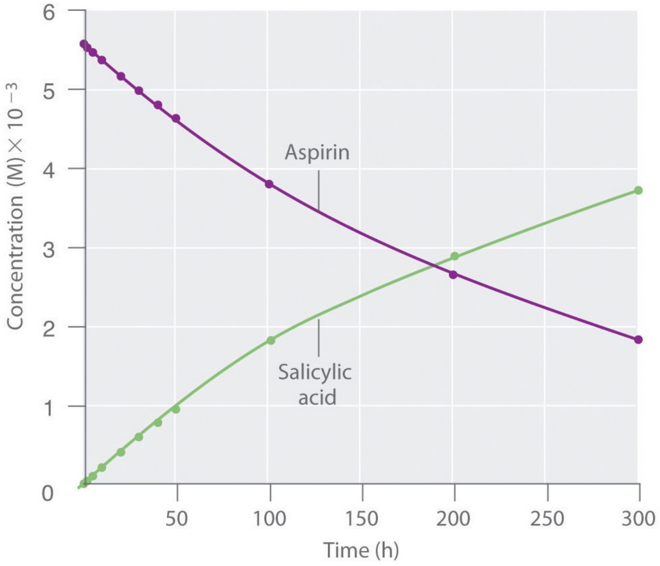


Figure 18.1.3: The Hydrolysis of Aspirin. This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid.

Graph of concentration against time in hours. The purple line is aspirin. The green line is salicylic acid.

The **average reaction rate** for a given time interval can be calculated from the concentrations of either the reactant or one of the products at the beginning of the interval (time = t_0) and at the end of the interval (t_1). Using salicylic acid, the reaction rate for the interval between t = 0 h and t = 2.0 h (recall that change is always calculated as final minus initial) is calculated as follows:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= \frac{[\text{salicyclic acid}]_2 - [\text{salicyclic acid}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= \frac{0.040\times10^{-3}\text{ M} - 0\text{ M}}{2.0\text{ h}} = 2.0\times10^{-5}\text{ M/h}\end{aligned}$$

The reaction rate can also be calculated from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= -\frac{[\text{aspirin}]_2 - [\text{aspirin}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= -\frac{(5.51\times10^{-3}\text{ M}) - (5.55\times10^{-3}\text{ M})}{2.0\text{ h}} \\ &= 2\times10^{-5}\text{ M/h}\end{aligned}$$

If the reaction rate is calculated during the last interval given in Table 18.1.1(the interval between 200 h and 300 h after the start of the reaction), the reaction rate is significantly slower than it was during the first interval (t = 0–2.0 h):

$$\begin{aligned}\text{rate}_{(t=200-300\text{h})} &= \frac{[\text{salicyclic acid}]_{300} - [\text{salicyclic acid}]_{200}}{300\text{ h} - 200\text{ h}} \\ &= -\frac{(3.73\times10^{-3}\text{ M}) - (2.91\times10^{-3}\text{ M})}{100\text{ h}} \\ &= 8.2\times10^{-6}\text{ M/h}\end{aligned}$$

Calculating the Reaction Rate of Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Consider a reaction in which the coefficients are not all the same, the fermentation of sucrose to ethanol and carbon dioxide:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \rightarrow 4C_2H_5OH(aq) + 4CO_2(g) \tag{18.1.2}$$

The coefficients indicate that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, the reaction rate can be found from the change in the concentration of any reactant or product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and, as explained in Chapter 10, the volume of CO_2 gas formed depends on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

$$\frac{\Delta[C_2H_5OH]}{\Delta t} = -\frac{4\Delta[\text{sucrose}]}{\Delta t} \tag{18.1.3}$$

The concentration of the reactant—in this case sucrose—*decreases* with time, so the value of Δ[sucrose] is negative. Consequently, a minus sign is inserted in front of Δ[sucrose] in Equation 18.1.3 so the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product with the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 18.1.2) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta[C_2H_5OH]}{\Delta t}\right) \tag{18.1.4}$$

✓ Example 18.1.1: Decomposition Reaction I

Consider the thermal decomposition of gaseous N_2O_5 to NO_2 and O_2 via the following equation:

$$2N_2O_5(g) \xrightarrow{\Delta} 4NO_2(g) + O_2(g)$$

Write expressions for the reaction rate in terms of the rates of change in the concentrations of the reactant and each product with time.

Given: balanced chemical equation

Asked for: reaction rate expressions

Strategy:

A. Choose the species in the equation that has the smallest coefficient. Then write an expression for the rate of change of that species with time.
B. For the remaining species in the equation, use molar ratios to obtain equivalent expressions for the reaction rate.

Solution

A Because O_2 has the smallest coefficient in the balanced chemical equation for the reaction, define the reaction rate as the rate of change in the concentration of O_2 and write that expression.

B The balanced chemical equation shows that 2 mol of N_2O_5 must decompose for each 1 mol of O_2 produced and that 4 mol of NO_2 are produced for every 1 mol of O_2 produced. The molar ratios of O_2 to N_2O_5 and to NO_2 are thus 1:2 and 1:4, respectively. This means that the rate of change of $[N_2O_5]$ and $[NO_2]$ must be divided by its stoichiometric coefficient to obtain equivalent expressions for the reaction rate. For example, because NO_2 is produced at four times the rate of O_2, the rate of production of NO_2 is divided by 4. The reaction rate expressions are as follows:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

? Exercise 18.1.1: Contact Process I

The contact process is used in the manufacture of sulfuric acid. A key step in this process is the reaction of SO_2 with O_2 to produce SO_3.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.

Answer

$$\text{rate} = -\frac{\Delta[\mathrm{O_2}]}{\Delta t} = -\frac{\Delta[\mathrm{SO_2}]}{2\Delta t} = \frac{\Delta[\mathrm{SO_3}]}{2\Delta t}$$

Instantaneous Rates of Reaction

The **instantaneous rate** of a reaction is the reaction rate at any given point in time. As the period of time used to calculate an average rate of a reaction becomes shorter and shorter, the average rate approaches the instantaneous rate. Comparing this to calculus, the instantaneous rate of a reaction at a given time corresponds to the slope of a line tangent to the concentration-versus-time curve at that point—that is, the derivative of concentration with respect to time.

The distinction between the instantaneous and average rates of a reaction is similar to the distinction between the actual speed of a car at any given time on a trip and the average speed of the car for the entire trip. Although the car may travel for an extended period at 65 mph on an interstate highway during a long trip, there may be times when it travels only 25 mph in construction zones or 0 mph if you stop for meals or gas. The average speed on the trip may be only 50 mph, whereas the instantaneous speed on the interstate at a given moment may be 65 mph. Whether the car can be stopped in time to avoid an accident depends on its instantaneous speed, not its average speed. There are important differences between the speed of a car during a trip and the speed of a chemical reaction, however. The speed of a car may vary unpredictably over the length of a trip, and the initial part of a trip is often one of the slowest. In a chemical reaction, the initial interval typically has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

> *Chemical kinetics generally focuses on one particular instantaneous rate, which is the initial reaction rate, t = 0. Initial rates are determined by measuring the reaction rate at various times and then extrapolating a plot of rate versus time to t = 0.*

✓ Example 18.1.2: Decomposition Reaction II

Using the reaction shown in Example 18.1.1, calculate the reaction rate from the following data taken at 56°C:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

calculate the reaction rate from the following data taken at 56°C:

Time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
240	0.0388	0.0314	0.00792
600	0.0197	0.0699	0.0175

Given: balanced chemical equation and concentrations at specific times

Asked for: reaction rate

Strategy:

A. Using the equations in Example 18.1.1, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.
B. Substitute the value for the time interval into the equation. Make sure your units are consistent.

Solution

A Calculate the reaction rate in the interval between t_1 = 240 s and t_2 = 600 s. From Example 18.1.1, the reaction rate can be evaluated using any of three expressions:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

Subtracting the initial concentration from the final concentration of N_2O_5 and inserting the corresponding time interval into the rate expression for N_2O_5,

$$\text{rate} = -\frac{\Delta[N_2O_5]}{2\Delta t} = -\frac{[N_2O_5]_{600} - [N_2O_5]_{240}}{2(600\text{ s} - 240\text{ s})}$$

B Substituting actual values into the expression,

$$\text{rate} = -\frac{0.0197\text{ M} - 0.0388\text{ M}}{2(360\text{ s})} = 2.65 \times 10^{-5}\text{ M/s}$$

Similarly, NO_2 can be used to calculate the reaction rate:

$$\text{rate} = \frac{\Delta[NO_2]}{4\Delta t} = \frac{[NO_2]_{600} - [NO_2]_{240}}{4(600\text{ s} - 240\text{ s})} = \frac{0.0699\text{ M} - 0.0314\text{ M}}{4(360\text{ s})} = 2.67 \times 10^{-5}\text{ M/s}$$

Allowing for experimental error, this is the same rate obtained using the data for N_2O_5. The data for O_2 can also be used:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{[O_2]_{600} - [O_2]_{240}}{600\text{ s} - 240\text{ s}} = \frac{0.0175\text{ M} - 0.00792\text{ M}}{360\text{ s}} = 2.66 \times 10^{-5}\text{ M/s}$$

Again, this is the same value obtained from the N_2O_5 and NO_2 data. Thus, the reaction rate does not depend on which reactant or product is used to measure it.

? Exercise 18.1.2: Contact Process II

Using the data in the following table, calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

Time (s)	$[SO_2]$ (M)	$[O_2]$ (M)	$[SO_3]$ (M)
300	0.0270	0.0500	0.0072
720	0.0194	0.0462	0.0148

Answer:

9.0×10^{-6} M/s

Summary

In this Module, the quantitative determination of a reaction rate is demonstrated. Reaction rates can be determined over particular time intervals or at a given point in time. A rate law describes the relationship between reactant rates and reactant concentrations. Reaction rates are reported as either the average rate over a period of time or as the instantaneous rate at a single time. Reaction rates can be determined over particular time intervals or at a given point in time.

- General definition of rate for A → B:

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t}$$

18.2: Rate Laws

Learning Objectives

- To apply rate laws to zeroth, first and second order reactions.

Either the differential rate law or the integrated rate law can be used to determine the reaction order from experimental data. Often, the exponents in the rate law are the positive integers: 1 and 2 or even 0. Thus the reactions are zeroth, first, or second order in each reactant. The common patterns used to identify the reaction order are described in this section, where we focus on characteristic types of differential and integrated rate laws and how to determine the reaction order from experimental data. The learning objective of this Module is to know how to determine the reaction order from experimental data.

Zeroth-Order Reactions

A **zeroth-order reaction** is one whose rate is independent of concentration; its differential rate law is

$$\text{rate} = k.$$

We refer to these reactions as zeroth order because we could also write their rate in a form such that the exponent of the reactant in the rate law is 0:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{reactant}]^0 = k(1) = k \tag{18.2.1}$$

Because rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of $-k$. The value of k is negative because the concentration of the reactant decreases with time. Conversely, a graph of the concentration of any product as a function of time is a straight line with a slope of k, a positive value.

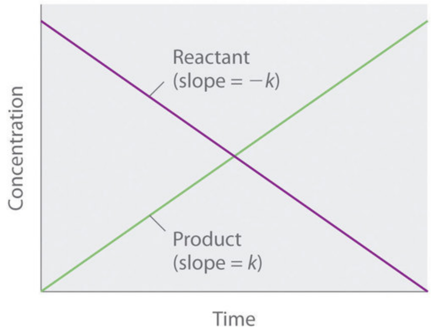


Figure 18.2.1: The graph of a zeroth-order reaction. The change in concentration of reactant and product with time produces a straight line.

Graph of concentration against time. The reactant is in purple and has a slope of minus k. The product is in green and has a slope of positive k.

The integrated rate law for a zeroth-order reaction also produces a straight line and has the general form

$$[A] = [A]_0 - kt \tag{18.2.2}$$

where $[A]_0$ is the initial concentration of reactant A. Equation 18.2.2has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = [A]$, $mx = -kt$, and $b = [A]_0$.)

Units

In a zeroth-order reaction, the rate constant must have the same units as the reaction rate, typically moles per liter per second.

Although it may seem counterintuitive for the reaction rate to be independent of the reactant concentration(s), such reactions are rather common. They occur most often when the reaction rate is determined by available surface area. An example is the decomposition of N_2O on a platinum (Pt) surface to produce N_2 and O_2, which occurs at temperatures ranging from 200°C to 400°C:

$$2N_2O(g) \xrightarrow{Pt} 2N_2(g) + O_2(g) \tag{18.2.3}$$

Without a platinum surface, the reaction requires temperatures greater than 700°C, but between 200°C and 400°C, the only factor that determines how rapidly N_2O decomposes is the amount of Pt surface available (not the amount of Pt). As long as there is enough N_2O to react with the entire Pt surface, doubling or quadrupling the N_2O concentration will have no effect on the reaction rate. At very low concentrations of N_2O, where there are not enough molecules present to occupy the entire available Pt surface, the reaction rate is dependent on the N_2O concentration. The reaction rate is as follows:

$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[N_2O]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[N_2]}{\Delta t}\right) = \frac{\Delta[O_2]}{\Delta t} = k[N_2O]^0 = k \tag{18.2.4}$$

Thus the rate at which N_2O is consumed and the rates at which N_2 and O_2 are produced are independent of concentration. As shown in Figure $18.2.2$, the change in the concentrations of all species with time is linear. Most important, the exponent (0) corresponding to the N_2O concentration in the experimentally derived rate law is not the same as the reactant's stoichiometric coefficient in the balanced chemical equation (2). For this reaction, as for all others, the rate law must be determined experimentally.

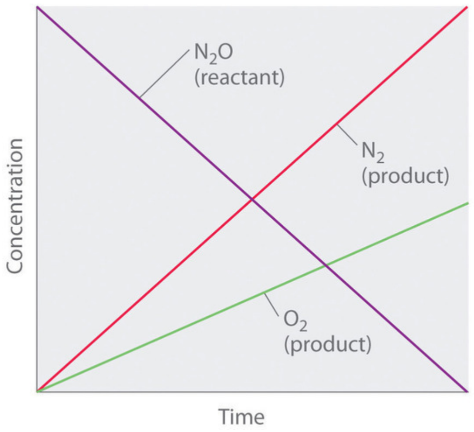
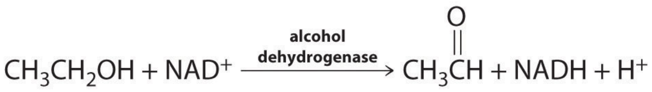


Figure 18.2.2: A Zeroth-Order Reaction. This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface. The change in the concentrations of all species with time is linear.

Graph of concentration against time. N2O is the reactant is graphed in purple. O2 is one of the products and is graphed in green. The second product is N2 which is graphed in red

A zeroth-order reaction that takes place in the human liver is the oxidation of ethanol (from alcoholic beverages) to acetaldehyde, catalyzed by the **enzyme** alcohol dehydrogenase. At high ethanol concentrations, this reaction is also a zeroth-order reaction. The overall reaction equation is



$$CH_3CH_2OH + NAD^+ \xrightarrow{\text{alcohol dehydrogenase}} CH_3\overset{O}{\overset{\|}{C}}H + NADH + H^+$$

Figure 18.2.2

where \ce{NAD^{+}}\) (nicotinamide adenine dinucleotide) and $NADH$ (reduced nicotinamide adenine dinucleotide) are the oxidized and reduced forms, respectively, of a species used by all organisms to transport electrons. When an alcoholic beverage is consumed, the ethanol is rapidly absorbed into the blood. Its concentration then decreases at a constant rate until it reaches zero (Figure $18.2.3a$). An average 70 kg person typically takes about 2.5 h to oxidize the 15 mL of ethanol contained in a single 12 oz can of beer, a 5 oz glass of wine, or a shot of distilled spirits (such as whiskey or brandy). The actual rate, however, varies a great deal from person to person, depending on body size and the amount of alcohol dehydrogenase in the liver. The reaction rate does not increase if a greater quantity of alcohol is consumed over the same period of time because the reaction rate is determined only by the amount of enzyme present in the liver. Contrary to popular belief, the caffeine in coffee is ineffective at catalyzing the oxidation of ethanol. When the ethanol has been completely oxidized and its concentration drops to essentially zero, the rate of oxidation also drops rapidly (part (b) in Figure $18.2.3$).

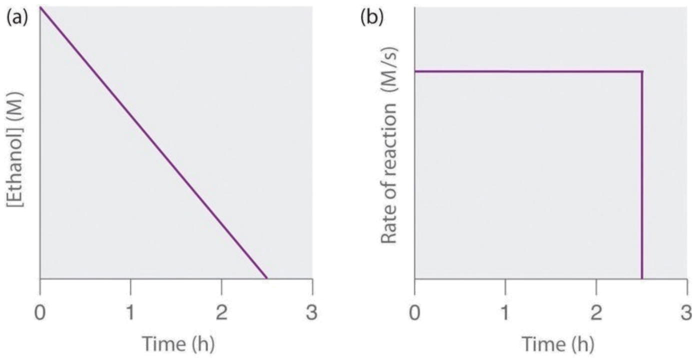


Figure 18.2.3: The Catalyzed Oxidation of Ethanol (a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point the reaction rate drops to zero.

These examples illustrate two important points:

1. In a zeroth-order reaction, the reaction rate does not depend on the reactant concentration.
2. A linear change in concentration with time is a clear indication of a zeroth-order reaction.

First-Order Reactions

In a **first-order reaction**, the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form A → products. The differential rate for a first-order reaction is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}] \tag{18.2.5}$$

If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per liter per second, the units of a first-order rate constant are reciprocal seconds (s^{-1}).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

$$[A] = [A]_0 e^{-kt} \tag{18.2.6}$$

where $[A]_0$ is the initial concentration of reactant A at $t = 0$; k is the rate constant; and e is the base of the natural logarithms, which has the value 2.718 to three decimal places. Recall that an integrated rate law gives the relationship between reactant concentration and time. Equation 18.2.6 predicts that the concentration of A will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side of Equation 18.2.6 and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and t:

$$\ln[A] = \ln[A]_0 - kt \tag{18.2.7}$$

Because Equation 18.2.7 has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = \ln[A]$ and $b = \ln[A]_0$, a plot of $\ln[A]$ versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$. Either the differential rate law (Equation 18.2.5) or the integrated rate law (Equation 18.2.7) can be used to determine whether a particular reaction is first order.

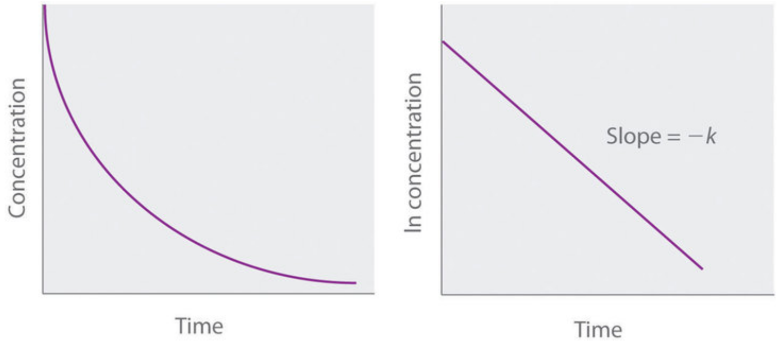


Figure 18.2.4: Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

First-order reactions are very common. One reaction that exhibits apparent first-order kinetics is the hydrolysis of the anticancer drug cisplatin. Cisplatin, the first “inorganic” anticancer drug to be discovered, is unique in its ability to cause complete remission of the relatively rare, but deadly cancers of the reproductive organs in young adults. The structures of cisplatin and its hydrolysis product are as follows:

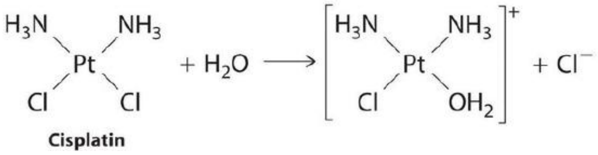


Figure 18.2.5: Cis-platin reaction with water.

Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure 18.2.5 is important because cisplatin, the form in which the drug is administered, is not the form in which the drug is active. Instead, at least one chloride ion must be replaced by water to produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell division and tumor growth. Consequently, the kinetics of the reaction in Figure 18.2.4 have been studied extensively to find ways of maximizing the concentration of the active species.

> *If a plot of reactant concentration versus time is not linear but a plot of the natural logarithm of reactant concentration versus time is linear, then the reaction is first order.*

The rate law and reaction order of the hydrolysis of cisplatin are determined from experimental data, such as those displayed in Table 18.2.1. The table lists initial rate data for four experiments in which the reaction was run at pH 7.0 and 25°C but with different initial concentrations of cisplatin.

Table 18.2.1: Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C

Experiment	$[\text{Cisplatin}]_0$ (M)	Initial Rate (M/min)
1	0.0060	9.0×10^{-6}
2	0.012	1.8×10^{-5}
3	0.024	3.6×10^{-5}
4	0.030	4.5×10^{-5}

Because the reaction rate increases with increasing cisplatin concentration, we know this cannot be a zeroth-order reaction. Comparing Experiments 1 and 2 in Table 18.2.1 shows that the reaction rate doubles [(1.8×10^{-5} M/min) ÷ (9.0×10^{-6} M/min) = 2.0] when the concentration of cisplatin is doubled (from 0.0060 M to 0.012 M). Similarly, comparing Experiments 1 and 4 shows that the reaction rate increases by a factor of 5 [(4.5×10^{-5} M/min) ÷ (9.0×10^{-6} M/min) = 5.0] when the concentration of cisplatin is increased by a factor of 5 (from 0.0060 M to 0.030 M). Because the reaction rate is directly proportional to the concentration of the reactant, the exponent of the cisplatin concentration in the rate law must be 1, so the rate law is rate = $k[\text{cisplatin}]^1$. Thus the reaction is first order. Knowing this, we can calculate the rate constant using the differential rate law for a first-order reaction and the data in any row of Table 18.2.1. For example, substituting the values for Experiment 3 into Equation 18.2.5,

$$3.6 \times 10^{-5}\ \text{M/min} = k(0.024\ \text{M})$$

$$1.5 \times 10^{-3}\ \text{min}^{-1} = k$$

Knowing the rate constant for the hydrolysis of cisplatin and the rate constants for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with solutions that contain only the desired form of the drug.

✓ Example 18.2.1

At high temperatures, ethyl chloride produces HCl and ethylene by the following reaction:

$$\mathrm{CH_3CH_2Cl(g)} \xrightarrow{\Delta} \mathrm{HCl(g)} + \mathrm{C_2H_4(g)}$$

Using the rate data for the reaction at 650°C presented in the following table, calculate the reaction order with respect to the concentration of ethyl chloride and determine the rate constant for the reaction.

data for the reaction at 650°C

Experiment	$[CH_3CH_2Cl]_0$ (M)	Initial Rate (M/s)
1	0.010	1.6×10^{-8}
2	0.015	2.4×10^{-8}
3	0.030	4.8×10^{-8}
4	0.040	6.4×10^{-8}

Given: balanced chemical equation, initial concentrations of reactant, and initial rates of reaction

Asked for: reaction order and rate constant

Strategy:

A. Compare the data from two experiments to determine the effect on the reaction rate of changing the concentration of a species.
B. Compare the observed effect with behaviors characteristic of zeroth- and first-order reactions to determine the reaction order. Write the rate law for the reaction.

C Use measured concentrations and rate data from any of the experiments to find the rate constant.

Solution

The reaction order with respect to ethyl chloride is determined by examining the effect of changes in the ethyl chloride concentration on the reaction rate.

A Comparing Experiments 2 and 3 shows that doubling the concentration doubles the reaction rate, so the reaction rate is proportional to $[CH_3CH_2Cl]$. Similarly, comparing Experiments 1 and 4 shows that quadrupling the concentration quadruples the reaction rate, again indicating that the reaction rate is directly proportional to $[CH_3CH_2Cl]$.

B This behavior is characteristic of a first-order reaction, for which the rate law is rate = $k[CH_3CH_2Cl]$.

C We can calculate the rate constant (k) using any row in the table. Selecting Experiment 1 gives the following:

$$1.60 \times 10^{-8}\ \text{M/s} = k(0.010\ \text{M})$$

$$1.6 \times 10^{-6}\ \text{s}^{-1} = k$$

? Exercise 18.2.1

Sulfuryl chloride (SO_2Cl_2) decomposes to SO_2 and Cl_2 by the following reaction:

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

Data for the reaction at 320°C are listed in the following table. Calculate the reaction order with regard to sulfuryl chloride and determine the rate constant for the reaction.

Data for the reaction at 320°C

Experiment	$[SO_2Cl_2]_0$ (M)	Initial Rate (M/s)
1	0.0050	1.10×10^{-7}
2	0.0075	1.65×10^{-7}
3	0.0100	2.20×10^{-7}
4	0.0125	2.75×10^{-7}

Answer

first order; $k = 2.2 \times 10^{-5}\ s^{-1}$

We can also use the integrated rate law to determine the reaction rate for the hydrolysis of cisplatin. To do this, we examine the change in the concentration of the reactant or the product as a function of time at a single initial cisplatin concentration. Figure $18.2.6a$ shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C.

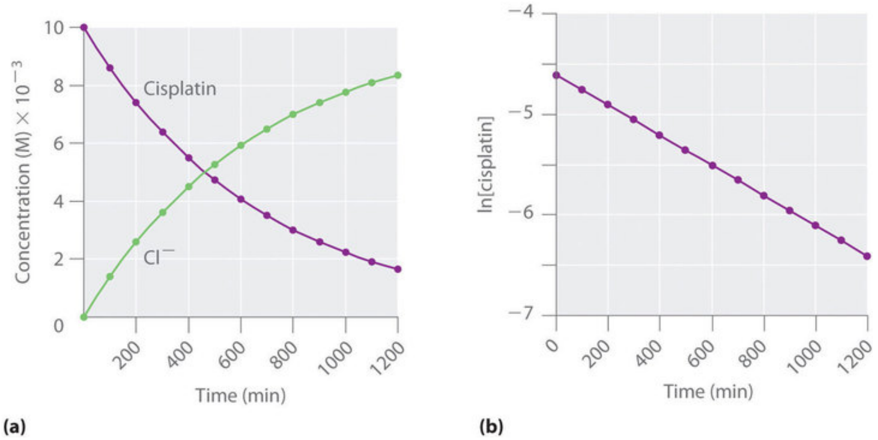


Figure 18.2.6: The Hydrolysis of Cisplatin, a First-Order Reaction. These plots show hydrolysis of cisplatin at pH 7.0 and 25°C as (a) the experimentally determined concentrations of cisplatin and chloride ions versus time and (b) the natural logarithm of the cisplatin concentration versus time. The straight line in (b) is expected for a first-order reaction.

The concentration of cisplatin decreases smoothly with time, and the concentration of chloride ion increases in a similar way. When we plot the natural logarithm of the concentration of cisplatin versus time, we obtain the plot shown in part (b) in Figure $18.2.6$. The straight line is consistent with the behavior of a system that obeys a first-order rate law. We can use any two points on the line to calculate the slope of the line, which gives us the rate constant for the reaction. Thus taking the points from part (a) in Figure $18.2.6$ for t = 100 min ([cisplatin] = 0.0086 M) and t = 1000 min ([cisplatin] = 0.0022 M),

$$\begin{aligned} \text{slope} &= \frac{\ln[\text{cisplatin}]_{1000} - \ln[\text{cisplatin}]_{100}}{1000\text{ min} - 100\text{ min}} \\ -k &= \frac{\ln 0.0022 - \ln 0.0086}{1000\text{ min} - 100\text{ min}} = \frac{-6.12 - (-4.76)}{900\text{ min}} = -1.51 \times 10^{-3}\text{ min}^{-1} \\ k &= 1.5 \times 10^{-3}\text{ min}^{-1} \end{aligned}$$

The slope is negative because we are calculating the rate of disappearance of cisplatin. Also, the rate constant has units of min^{-1} because the times plotted on the horizontal axes in parts (a) and (b) in Figure $18.2.6$ are in minutes rather than seconds.

The reaction order and the magnitude of the rate constant we obtain using the integrated rate law are exactly the same as those we calculated earlier using the differential rate law. This must be true if the experiments were carried out under the same conditions.

Video Example Using the First-Order Integrated Rate Law Equation:

Example Using the First-Order Integrated Rate Law Equation(opens in new window) [youtu.be]

✓ Example 18.2.2

If a sample of ethyl chloride with an initial concentration of 0.0200 M is heated at 650°C, what is the concentration of ethyl chloride after 10 h? How many hours at 650°C must elapse for the concentration to decrease to 0.0050 M (k = 1.6 × 10^{-6} s^{-1}) ?

Given: initial concentration, rate constant, and time interval

Asked for: concentration at specified time and time required to obtain particular concentration

Strategy:

A. Substitute values for the initial concentration ($[A]_0$) and the calculated rate constant for the reaction (k) into the integrated rate law for a first-order reaction. Calculate the concentration ([A]) at the given time t.
B. Given a concentration [A], solve the integrated rate law for time t.

Solution

The exponential form of the integrated rate law for a first-order reaction (Equation 18.2.6) is $[A] = [A]_0e^{-kt}$.

A Having been given the initial concentration of ethyl chloride ($[A]_0$) and having the rate constant of k = 1.6 × 10^{-6} s^{-1}, we can use the rate law to calculate the concentration of the reactant at a given time t. Substituting the known values into the integrated rate law,

$$\begin{aligned}
[\mathrm{CH_3CH_2Cl}]_{10\ \mathrm{h}} &= [\mathrm{CH_3CH_2Cl}]_0 e^{-kt} \\
&= 0.0200\ \mathrm{M}(e^{-(1.6\times10^{-6}\ \mathrm{s}^{-1})[(10\ \mathrm{h})(60\ \mathrm{min/h})(60\ \mathrm{s/min})]}) \\
&= 0.0189\ \mathrm{M}
\end{aligned}$$

We could also have used the logarithmic form of the integrated rate law (Equation 18.2.7):

$$\begin{aligned}
\ln[\mathrm{CH_3CH_2Cl}]_{10\,\mathrm{h}} &= \ln[\mathrm{CH_3CH_2Cl}]_0 - kt \\
&= \ln 0.0200 - (1.6 \times 10^{-6}\ \mathrm{s}^{-1})[(10\ \mathrm{h})(60\ \mathrm{min/h})(60\ \mathrm{s/min})] \\
&= -3.912 - 0.0576 = -3.970 \\
[\mathrm{CH_3CH_2Cl}]_{10\,\mathrm{h}} &= e^{-3.970}\ \mathrm{M} \\
&= 0.0189\ \mathrm{M}
\end{aligned}$$

B To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for t. Equation 18.2.7 gives the following:

$$\begin{aligned}\ln[\mathrm{CH_3CH_2Cl}]_t &= \ln[\mathrm{CH_3CH_2Cl}]_0 - kt \\ kt &= \ln[\mathrm{CH_3CH_2Cl}]_0 - \ln[\mathrm{CH_3CH_2Cl}]_t = \ln\frac{[\mathrm{CH_3CH_2Cl}]_0}{[\mathrm{CH_3CH_2Cl}]_t} \\ t &= \frac{1}{k}\left(\ln\frac{[\mathrm{CH_3CH_2Cl}]_0}{[\mathrm{CH_3CH_2Cl}]_t}\right) = \frac{1}{1.6\times10^{-6}\ \mathrm{s^{-1}}}\left(\ln\frac{0.0200\ \mathrm{M}}{0.0050\ \mathrm{M}}\right) \\ &= \frac{\ln 4.0}{1.6\times10^{-6}\ \mathrm{s^{-1}}} = 8.7\times10^{5}\ \mathrm{s} = 240\ \mathrm{h} = 2.4\times10^{2}\ \mathrm{h}\end{aligned}$$

? Exercise 18.2.2

In the exercise in Example 18.2.1, you found that the decomposition of sulfuryl chloride (SO_2Cl_2) is first order, and you calculated the rate constant at 320°C.

a. Use the form(s) of the integrated rate law to find the amount of SO_2Cl_2 that remains after 20 h if a sample with an original concentration of 0.123 M is heated at 320°C.
b. How long would it take for 90% of the SO_2Cl_2 to decompose?

Answer a

0.0252 M

Answer b

29 h

Second-Order Reactions

The simplest kind of **second-order reaction** is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form

$$2\ \mathrm{A} \rightarrow \text{products}\cdot$$

A second kind of second-order reaction has a reaction rate that is proportional to the product of the concentrations of two reactants. Such reactions generally have the form A + B → products. An example of the former is a dimerization reaction, in which two smaller molecules, each called a monomer, combine to form a larger molecule (a dimer).

The differential rate law for the simplest second-order reaction in which 2A → products is as follows:

$$\text{rate} = -\frac{\Delta[\mathrm{A}]}{2\Delta t} = k[\mathrm{A}]^2 \tag{18.2.8}$$

Consequently, doubling the concentration of A quadruples the reaction rate. For the units of the reaction rate to be moles per liter per second (M/s), the units of a second-order rate constant must be the inverse ($M^{-1}\cdot s^{-1}$). Because the units of molarity are expressed as mol/L, the unit of the rate constant can also be written as L(mol·s).

For the reaction 2A → products, the following integrated rate law describes the concentration of the reactant at a given time:

$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + kt \tag{18.2.9}$$

Because Equation 18.2.9 has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[A]$ and $b = 1/[A]_0$, a plot of 1/[A] versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of $1/[A]_0$.

> *Second-order reactions generally have the form 2A → products or A + B → products.*

Video Discussing the Second-Order Integrated Rate Law Equation: Second-Order Integrated Rate Law Equation(opens in new window) [youtu.be]

Simple second-order reactions are common. In addition to dimerization reactions, two other examples are the decomposition of NO_2 to NO and O_2 and the decomposition of HI to I_2 and H_2. Most examples involve simple inorganic molecules, but there are organic examples as well. We can follow the progress of the reaction described in the following paragraph by monitoring the decrease in the intensity of the red color of the reaction mixture.

Many cyclic organic compounds that contain two carbon–carbon double bonds undergo a dimerization reaction to give complex structures. One example is as follows:

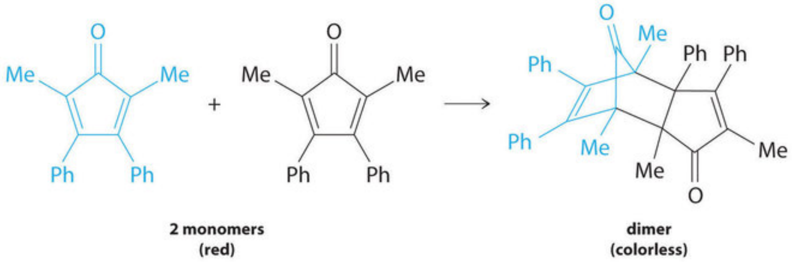


Figure 18.2.7

For simplicity, we will refer to this reactant and product as “monomer” and “dimer,” respectively. The systematic name of the monomer is 2,5-dimethyl-3,4-diphenylcyclopentadienone. The systematic name of the dimer is the name of the monomer followed by “dimer.” Because the monomers are the same, the general equation for this reaction is 2A → product. This reaction represents an important class of organic reactions used in the pharmaceutical industry to prepare complex carbon skeletons for the synthesis of drugs. Like the first-order reactions studied previously, it can be analyzed using either the differential rate law (Equation 18.2.8) or the integrated rate law (Equation 18.2.9).

Table 18.2.2: Rates of Reaction as a Function of Monomer Concentration for an Initial Monomer Concentration of 0.0054 M

Time (min)	[Monomer] (M)	Instantaneous Rate (M/min)
10	0.0044	8.0×10^{-5}
26	0.0034	5.0×10^{-5}
44	0.0027	3.1×10^{-5}
70	0.0020	1.8×10^{-5}
120	0.0014	8.0×10^{-6}

To determine the differential rate law for the reaction, we need data on how the reaction rate varies as a function of monomer concentrations, which are provided in Table 18.2.2 From the data, we see that the reaction rate is not independent of the monomer concentration, so this is not a zeroth-order reaction. We also see that the reaction rate is not proportional to the monomer concentration, so the reaction is not first order. Comparing the data in the second and fourth rows shows that the reaction rate decreases by a factor of 2.8 when the monomer concentration decreases by a factor of 1.7:

$$\frac{5.0\times 10^{-5}\ \mathrm{M/min}}{1.8\times 10^{-5}\ \mathrm{M/min}}=2.8 \quad \text{and} \quad \frac{3.4\times 10^{-3}\ \mathrm{M}}{2.0\times 10^{-3}\ \mathrm{M}}=1.7$$

Because $(1.7)^2 = 2.9 \approx 2.8$, the reaction rate is approximately proportional to the square of the monomer concentration.

$$\text{rate} \propto [\text{monomer}]^2$$

This means that the reaction is second order in the monomer. Using Equation 18.2.8 and the data from any row in Table 18.2.2, we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$\text{rate} = k[\mathrm{A}]^2 \tag{18.2.10}$$

$$8.0\times 10^{-5}\ \mathrm{M/min} = k(4.4\times 10^{-3}\ \mathrm{M})^2 \tag{18.2.11}$$

$$4.1\ \mathrm{M^{-1}\cdot min^{-1}} = k \tag{18.2.12}$$

We can also determine the reaction order using the integrated rate law. To do so, we use the decrease in the concentration of the monomer as a function of time for a single reaction, plotted in Figure 18.2.8a. The measurements show that the concentration of the monomer (initially 5.4×10^{-3} M) decreases with increasing time. This graph also shows that the reaction rate decreases smoothly with increasing time. According to the integrated rate law for a second-order reaction, a plot of 1/[monomer] versus t should be a straight line, as shown in Figure 18.2.8b. Any pair of points on the line can be used to calculate the slope, which is the second-order rate constant. In this example, $k = 4.1\ \mathrm{M^{-1}{\cdot}min^{-1}}$, which is consistent with the result obtained using the differential rate equation. Although in this example the stoichiometric coefficient is the same as the reaction order, this is not always the case. The reaction order must always be determined experimentally.

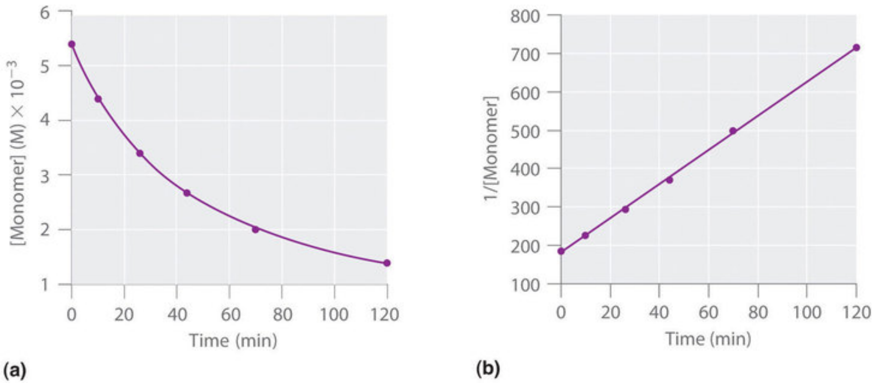


Figure 18.2.8: Dimerization of a Monomeric Compound, a Second-Order Reaction. These plots correspond to dimerization of the monomer in Figure 14.4.6 as (a) the experimentally determined concentration of monomer versus time and (b) 1/[monomer] versus time. The straight line in (b) is expected for a simple second-order reaction.

For two or more reactions of the same order, the reaction with the largest rate constant is the fastest. Because the units of the rate constants for zeroth-, first-, and second-order reactions are different, however, we cannot compare the magnitudes of rate constants for reactions that have different orders.

✓ Example 18.2.3

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.

$$2\mathrm{NO_2(g)} \xrightarrow{\Delta} 2\mathrm{NO(g)} + \mathrm{O_2(g)}$$

Experimental data for the reaction at 300°C and four initial concentrations of NO_2 are listed in the following table:

Experimental data for the reaction at 300°C and four initial concentrations of NO2

Experiment	$[NO_2]_0$ (M)	Initial Rate (M/s)
1	0.015	1.22×10^{-4}

Experiment	$[NO_2]_0$ (M)	Initial Rate (M/s)
2	0.010	5.40×10^{-5}
3	0.0080	3.46×10^{-5}
4	0.0050	1.35×10^{-5}

Determine the reaction order and the rate constant.

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: reaction order and rate constant

Strategy:

A. From the experiments, compare the changes in the initial reaction rates with the corresponding changes in the initial concentrations. Determine whether the changes are characteristic of zeroth-, first-, or second-order reactions.
B. Determine the appropriate rate law. Using this rate law and data from any experiment, solve for the rate constant (*k*).

Solution

A We can determine the reaction order with respect to nitrogen dioxide by comparing the changes in NO_2 concentrations with the corresponding reaction rates. Comparing Experiments 2 and 4, for example, shows that doubling the concentration quadruples the reaction rate $[(5.40 \times 10^{-5}) \div (1.35 \times 10^{-5}) = 4.0]$, which means that the reaction rate is proportional to $[NO_2]^2$. Similarly, comparing Experiments 1 and 4 shows that tripling the concentration increases the reaction rate by a factor of 9, again indicating that the reaction rate is proportional to $[NO_2]^2$. This behavior is characteristic of a second-order reaction.

B We have rate = $k[NO_2]^2$. We can calculate the rate constant (*k*) using data from any experiment in the table. Selecting Experiment 2, for example, gives the following:

$$\begin{aligned} \text{rate} &= k[\text{NO}_2]^2 \\ 5.40 \times 10^{-5} \text{ M/s} &= k(0.010 \text{ M})^2 \\ 0.54 \text{ M}^{-1} \cdot \text{s}^{-1} &= k \end{aligned}$$

? Exercise 18.2.3

When the highly reactive species HO_2 forms in the atmosphere, one important reaction that then removes it from the atmosphere is as follows:

$$2HO_{2(g)} \rightarrow H_2O_{2(g)} + O_{2(g)}$$

The kinetics of this reaction have been studied in the laboratory, and some initial rate data at 25°C are listed in the following table:

Some initial rate data at 25°C

Experiment	$[HO_2]_0$ (M)	Initial Rate (M/s)
1	1.1×10^{-8}	1.7×10^{-7}
2	2.5×10^{-8}	8.8×10^{-7}
3	3.4×10^{-8}	1.6×10^{-6}
4	5.0×10^{-8}	3.5×10^{-6}

Determine the reaction order and the rate constant.

Answer

second order in HO_2; $k = 1.4 \times 10^9$ $M^{-1} \cdot s^{-1}$

If a plot of reactant concentration versus time is **not** linear, but a plot of 1/(reactant concentration) versus time is linear, then the reaction is second order.

✓ Example 18.2.4

If a flask that initially contains 0.056 M NO_2 is heated at 300°C, what will be the concentration of NO_2 after 1.0 h? How long will it take for the concentration of NO_2 to decrease to 10% of the initial concentration? Use the integrated rate law for a second-order reaction (Equation 18.2.9) and the rate constant calculated above.

Given: balanced chemical equation, rate constant, time interval, and initial concentration

Asked for: final concentration and time required to reach specified concentration

Strategy:

A. Given k, t, and $[A]_0$, use the integrated rate law for a second-order reaction to calculate [A].
B. Setting [A] equal to 1/10 of $[A]_0$, use the same equation to solve for t.

Solution

A We know k and $[NO_2]_0$, and we are asked to determine $[NO_2]$ at t = 1 h (3600 s). Substituting the appropriate values into Equation 18.2.9,

$$\begin{aligned}\frac{1}{[NO_2]_{3600}} &= \frac{1}{[NO_2]_0} + kt \\ &= \frac{1}{0.056\ M} + [(0.54\ M^{-1}\cdot s^{-1})(3600\ s)] \\ &= 2.0 \times 10^3\ M^{-1}\end{aligned}$$

Thus $[NO_2]_{3600} = 5.1 \times 10^{-4}$ M.

B In this case, we know k and $[NO_2]_0$, and we are asked to calculate at what time $[NO_2] = 0.1[NO_2]_0 = 0.1(0.056\ M) = 0.0056$ M. To do this, we solve Equation 18.2.9 for t, using the concentrations given.

$$\begin{aligned}t &= \frac{(1/[NO_2]) - (1/[NO_2]_0)}{k} \\ &= \frac{(1/0.0056\ M) - (1/0.056\ M)}{0.54\ M^{-1}\cdot s^{-1}} \\ &= 3.0 \times 10^2\ s = 5.0\ min\end{aligned}$$

NO_2 decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

? Exercise 18.2.4

In the previous exercise, you calculated the rate constant for the decomposition of HO_2 as $k = 1.4 \times 10^9\ M^{-1}\cdot s^{-1}$. This high rate constant means that HO_2 decomposes rapidly under the reaction conditions given in the problem. In fact, the HO_2 molecule is so reactive that it is virtually impossible to obtain in high concentrations. Given a 0.0010 M sample of HO_2, calculate the concentration of HO_2 that remains after 1.0 h at 25°C. How long will it take for 90% of the HO_2 to decompose? Use the integrated rate law for a second-order reaction (Equation 18.2.9) and the rate constant calculated in the exercise in Example 18.2.3.

Answer

2.0×10^{-13} M; 6.4×10^{-6} s

In addition to the simple second-order reaction and rate law we have just described, another very common second-order reaction has the general form $A + B \rightarrow products$, in which the reaction is first order in A and first order in B. The differential rate law for this reaction is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{\Delta[\text{B}]}{\Delta t} = k[\text{A}][\text{B}]$$

Because the reaction is first order both in A and in B, it has an overall reaction order of 2. (The integrated rate law for this reaction is rather complex, so we will not describe it.) We can recognize second-order reactions of this sort because the reaction rate is proportional to the concentrations of each reactant.

Summary

The reaction rate of a zeroth-order reaction is independent of the concentration of the reactants. The reaction rate of a first-order reaction is directly proportional to the concentration of one reactant. The reaction rate of a simple second-order reaction is proportional to the square of the concentration of one reactant. Knowing the rate law of a reaction gives clues to the reaction mechanism.

- **zeroth-order reaction:**

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k$$

$$[A] = [A]_0 - kt$$

- **first-order reaction**:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]$$

$$[A] = [A]_0 e^{-kt}$$

$$\ln[A] = \ln[A]_0 - kt$$

- **second-order reaction:**

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^2$$

$$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + kt$$

18.3: Reaction Mechanisms

Learning Objectives

- To determine the individual steps of a simple reaction.

One of the major reasons for studying chemical kinetics is to use measurements of the macroscopic properties of a system, such as the rate of change in the concentration of reactants or products with time, to discover the sequence of events that occur at the molecular level during a reaction. This molecular description is the mechanism of the reaction; it describes how individual atoms, ions, or molecules interact to form particular products. The stepwise changes are collectively called the reaction mechanism.

In an internal combustion engine, for example, isooctane reacts with oxygen to give carbon dioxide and water:

$$2\,\mathrm{C_8H_{18}(l)} + 25\,\mathrm{O_2(g)} \longrightarrow 16\,\mathrm{CO_2(g)} + 18\,\mathrm{H_2O(g)} \tag{18.3.1}$$

For this reaction to occur in a single step, 25 dioxygen molecules and 2 isooctane molecules would have to collide simultaneously and be converted to 34 molecules of product, which is very unlikely. It is more likely that a complex series of reactions takes place in a stepwise fashion. Each individual reaction, which is called an **elementary reaction**, involves one, two, or (rarely) three atoms, molecules, or ions. The overall sequence of elementary reactions is the **mechanism** of the reaction. The sum of the individual steps, or elementary reactions, in the mechanism must give the balanced chemical equation for the overall reaction.

> *The overall sequence of elementary reactions is the mechanism of the reaction.*

Molecularity and the Rate-Determining Step

To demonstrate how the analysis of elementary reactions helps us determine the overall reaction mechanism, we will examine the much simpler reaction of carbon monoxide with nitrogen dioxide.

$$\mathrm{NO_2(g)} + \mathrm{CO(g)} \longrightarrow \mathrm{NO(g)} + \mathrm{CO_2(g)} \tag{18.3.2}$$

From the balanced chemical equation, one might expect the reaction to occur via a collision of one molecule of $\mathrm{NO_2}$ with a molecule of CO that results in the transfer of an oxygen atom from nitrogen to carbon. The experimentally determined rate law for the reaction, however, is as follows:

$$rate = k[\mathrm{NO_2}]^2 \tag{18.3.3}$$

The fact that the reaction is second order in $[\mathrm{NO_2}]$ and independent of $[\mathrm{CO}]$ tells us that it does not occur by the simple collision model outlined previously. If it did, its predicted rate law would be

$$rate = k[\mathrm{NO_2}][\mathrm{CO}].$$

The following two-step mechanism is consistent with the rate law if step 1 is much slower than step 2:

two-step mechanism

step 1	$\mathrm{NO_2 + NO_2 \xrightarrow{slow} NO_3 + NO}$	elementary reaction
step 2	$\underline{\mathrm{NO_3 + CO \rightarrow NO_2 + CO_2}}$	elementary reaction
sum	$\mathrm{NO_2 + CO \rightarrow NO + CO_2}$	overall reaction

According to this mechanism, the overall reaction occurs in two steps, or elementary reactions. Summing steps 1 and 2 and canceling on both sides of the equation gives the overall balanced chemical equation for the reaction. The $\mathrm{NO_3}$ molecule is an **intermediate** in the reaction, a species that does not appear in the balanced chemical equation for the overall reaction. It is formed as a product of the first step but is consumed in the second step.

> *The sum of the elementary reactions in a reaction mechanism* ***must*** *give the overall balanced chemical equation of the reaction.*

Using Molecularity to Describe a Rate Law

The **molecularity** of an elementary reaction is the number of molecules that collide during that step in the mechanism. If there is only a single reactant molecule in an elementary reaction, that step is designated as **unimolecular**; if there are two reactant molecules, it is **bimolecular**; and if there are three reactant molecules (a relatively rare situation), it is **termolecular**. Elementary reactions that involve the simultaneous collision of more than three molecules are highly improbable and have never been observed experimentally. (To understand why, try to make three or more marbles or pool balls collide with one another simultaneously!)

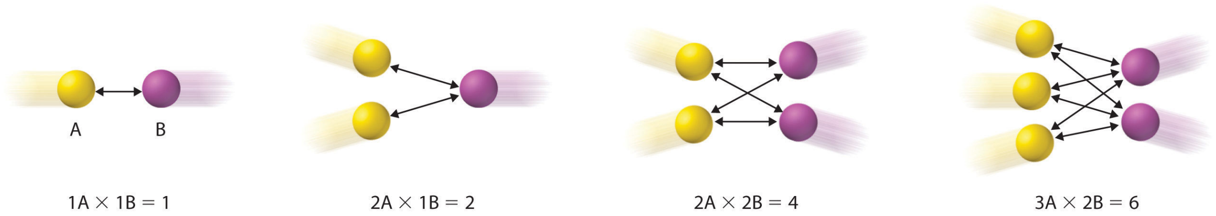


Figure 18.3.1: The Basis for Writing Rate Laws of Elementary Reactions. This diagram illustrates how the number of possible collisions per unit time between two reactant species, A and B, depends on the number of A and B particles present. The number of collisions between A and B particles increases as the product of the number of particles, not as the sum. This is why the rate law for an elementary reaction depends on the product of the concentrations of the species that collide in that step. (CC BY-NC-SA; anonymous)

Writing the rate law for an elementary reaction is straightforward because we know how many molecules must collide simultaneously for the elementary reaction to occur; hence the order of the elementary reaction is the same as its molecularity (Table $18.3.1$). In contrast, the rate law for the reaction cannot be determined from the balanced chemical equation for the overall reaction. The general rate law for a unimolecular elementary reaction (A → products) is

$$rate = k[A].$$

For bimolecular reactions, the reaction rate depends on the number of collisions per unit time, which is proportional to the product of the concentrations of the reactants, as shown in Figure $18.3.1$. For a bimolecular elementary reaction of the form A + B → products, the general rate law is

$$rate = k[A][B].$$

Table 18.3.1: Common Types of Elementary Reactions and Their Rate Laws

Elementary Reaction	Molecularity	Rate Law	Reaction Order
A → products	unimolecular	rate = k[A]	first
2A → products	bimolecular	rate = $k[A]^2$	second
A + B → products	bimolecular	rate = k[A][B]	second
2A + B → products	termolecular	rate = $k[A]^2[B]$	third
A + B + C → products	termolecular	rate = k[A][B][C]	third

> *For elementary reactions, the order of the elementary reaction is the same as its molecularity. In contrast, the rate law **cannot** be determined from the balanced chemical equation for the overall reaction (unless it is a single step mechanism and is therefore also an elementary step).*

Identifying the Rate-Determining Step

Note the important difference between writing rate laws for elementary reactions and the balanced chemical equation of the overall reaction. Because the balanced chemical equation does not necessarily reveal the individual elementary reactions by which the reaction occurs, we cannot obtain the rate law for a reaction from the overall balanced chemical equation alone. In fact, it is the rate law for the slowest overall reaction, which is the same as the rate law for the slowest step in the reaction mechanism, the **rate-determining step**, that must give the experimentally determined rate law for the overall reaction.This statement is true if one step is substantially slower than all the others, typically by a factor of 10 or more. If two or more slow steps have comparable rates, the experimentally determined rate laws can become complex. Our discussion is limited to reactions in which one step can be identified as being substantially slower than any other. The reason for this is that any process that occurs through a sequence of steps can take place no faster than the slowest step in the sequence. In an automotive assembly line, for example, a component cannot be used faster than it is produced. Similarly, blood pressure is regulated by the flow of blood through the smallest passages, the capillaries. Because movement through capillaries constitutes the rate-determining step in blood flow, blood pressure can be regulated by medications that cause the capillaries to contract or dilate. A chemical reaction that occurs via a series of elementary reactions can take place no faster than the slowest step in the series of reactions.

Rate-determining step. The phenomenon of a rate-determining step can be compared to a succession of funnels. The smallest-diameter funnel controls the rate at which the bottle is filled, whether it is the first or the last in the series. Pouring liquid into the first funnel faster than it can drain through the smallest results in an overflow. (CC BY-NC-SA; anonymous)

Look at the rate laws for each elementary reaction in our example as well as for the overall reaction.

rate laws for each elementary reaction in our example as well as for the overall reaction.

step 1	$NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$	rate $= k_1[NO_2]^2$ (predicted)
step 2	$\underline{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2}$	rate $= k_2[NO_3][CO]$ (predicted)
sum	$NO_2 + CO \xrightarrow{k} NO + CO_2$	rate $= k[NO_2]^2$ (observed)

The experimentally determined rate law for the reaction of NO_2 with CO is the same as the predicted rate law for step 1. This tells us that the first elementary reaction is the rate-determining step, so k for the overall reaction must equal k_1. That is, NO_3 is formed slowly in step 1, but once it is formed, it reacts very rapidly with CO in step 2.

Sometimes chemists are able to propose two or more mechanisms that are consistent with the available data. If a proposed mechanism predicts the wrong experimental rate law, however, the mechanism must be incorrect.

✓ Example 18.3.1: A Reaction with an Intermediate

In an alternative mechanism for the reaction of NO_2 with CO with N_2O_4 appearing as an intermediate.

alternative mechanism for the reaction of NO_2 with CO with N_2O_4 appearing as an intermediate.

step 1	$NO_2 + NO_2 \xrightarrow{k_1} N_2O_4$
step 2	$\underline{N_2O_4 + CO \xrightarrow{k_2} NO + NO_2 + CO_2}$
sum	$NO_2 + CO \rightarrow NO + CO_2$

Write the rate law for each elementary reaction. Is this mechanism consistent with the experimentally determined rate law (rate = $k[NO_2]^2$)?

Given: elementary reactions

Asked for: rate law for each elementary reaction and overall rate law

Strategy:

A. Determine the rate law for each elementary reaction in the reaction.
B. Determine which rate law corresponds to the experimentally determined rate law for the reaction. This rate law is the one for the rate-determining step.

Solution

A The rate law for step 1 is rate = $k_1[NO_2]^2$; for step 2, it is rate = $k_2[N_2O_4][CO]$.

B If step 1 is slow (and therefore the rate-determining step), then the overall rate law for the reaction will be the same: rate = $k_1[NO_2]^2$. This is the same as the experimentally determined rate law. Hence this mechanism, with N_2O_4 as an intermediate, and the one described previously, with NO_3 as an intermediate, are kinetically indistinguishable. In this case, further experiments are needed to distinguish between them. For example, the researcher could try to detect the proposed intermediates, NO_3 and N_2O_4, directly.

Exercise 18.3.1

Iodine monochloride (ICl) reacts with H_2 as follows:

$$2\,\mathrm{ICl(l)} + \mathrm{H_2(g)} \rightarrow 2\,\mathrm{HCl(g)} + \mathrm{I_2(s)}$$

The experimentally determined rate law is $rate = k[\mathrm{ICl}][\mathrm{H_2}]$. Write a two-step mechanism for this reaction using only bimolecular elementary reactions and show that it is consistent with the experimental rate law. (Hint: HI is an intermediate.)

Answer

Solutions to Exercise 14.6.1

step 1	$\mathrm{ICl} + \mathrm{H_2} \xrightarrow{k_1} \mathrm{HCl} + \mathrm{HI}$	$\mathrm{rate} = k_1[\mathrm{ICl}][\mathrm{H_2}]$ (slow)
step 2	$\underline{\mathrm{HI} + \mathrm{ICl} \xrightarrow{k_2} \mathrm{HCl} + \mathrm{I_2}}$	$\mathrm{rate} = k_2[\mathrm{HI}][\mathrm{ICl}]$ (fast)
sum	$2\mathrm{ICl} + \mathrm{H_2} \rightarrow 2\mathrm{HCl} + \mathrm{I_2}$	

This mechanism is consistent with the experimental rate law if the first step is the rate-determining step.

Example 18.3.2 : Nitrogen Oxide Reacting with Molecular Hydrogen

Assume the reaction between NO and H_2 occurs via a three-step process:

the reaction between NO and H_2 occurs via a three-step process

step 1	$\mathrm{NO} + \mathrm{NO} \xrightarrow{k_1} \mathrm{N_2O_2}$	(fast)
step 2	$\mathrm{N_2O_2} + \mathrm{H_2} \xrightarrow{k_2} \mathrm{N_2O} + \mathrm{H_2O}$	(slow)
step 3	$\mathrm{N_2O} + \mathrm{H_2} \xrightarrow{k_3} \mathrm{N_2} + \mathrm{H_2O}$	(fast)

Write the rate law for each elementary reaction, write the balanced chemical equation for the overall reaction, and identify the rate-determining step. Is the rate law for the rate-determining step consistent with the experimentally derived rate law for the overall reaction:

$$\mathrm{rate} = k[\mathrm{NO}]^2[\mathrm{H_2}]? \qquad \text{(observed)}$$

Answer

- Step 1: $rate = k_1[\mathrm{NO}]^2$
- Step 2: $rate = k_2[\mathrm{N_2O_2}][\mathrm{H_2}]$

- Step 3: $rate = k_3[\mathrm{N_2O}][\mathrm{H_2}]$

The overall reaction is then

$$2\,\mathrm{NO(g)} + 2\,\mathrm{H_2(g)} \longrightarrow \mathrm{N_2(g)} + 2\,\mathrm{H_2O(g)}$$

- Rate Determining Step : #2
- Yes, because the rate of formation of $[\mathrm{N_2O_2}] = k_1[\mathrm{NO}]^2$. Substituting $k_1[\mathrm{NO}]^2$ for $[\mathrm{N_2O_2}]$ in the rate law for step 2 gives the experimentally derived rate law for the overall chemical reaction, where $k = k_1k_2$.

Reaction Mechanism (Slow step followed by fast step): Reaction Mechanism (Slow step Followed by Fast Step)(opens in new window) [youtu.be] (opens in new window)

Summary

A balanced chemical reaction does not necessarily reveal either the individual elementary reactions by which a reaction occurs or its rate law. A reaction mechanism is the microscopic path by which reactants are transformed into products. Each step is an elementary reaction. Species that are formed in one step and consumed in another are intermediates. Each elementary reaction can be described in terms of its *molecularity*, the number of molecules that collide in that step. The slowest step in a reaction mechanism is the rate-determining step.

18.4: Reaction Mechanisms and Rate

note sure without book

18.5: Effect of Temperature on Reaction Rates

Learning Objectives

- To understand why and how chemical reactions occur.

It is possible to use kinetics studies of a chemical system, such as the effect of changes in reactant concentrations, to deduce events that occur on a microscopic scale, such as collisions between individual particles. Such studies have led to the collision model of chemical kinetics, which is a useful tool for understanding the behavior of reacting chemical species. The collision model explains why chemical reactions often occur more rapidly at higher temperatures. For example, the reaction rates of many reactions that occur at room temperature approximately double with a temperature increase of only 10°C. In this section, we will use the collision model to analyze this relationship between temperature and reaction rates. Before delving into the relationship between temperature and reaction rate, we must discuss three microscopic factors that influence the observed macroscopic reaction rates.

Microscopic Factor 1: Collisional Frequency

Central to collision model is that a chemical reaction can occur only when the reactant molecules, atoms, or ions collide. Hence, the observed rate is influence by the frequency of collisions between the reactants. The **collisional frequency** is the average rate in which two reactants collide for a given system and is used to express the average number of collisions per unit of time in a defined system. While deriving the collisional frequency (Z_{AB}) between two species in a gas is straightforward, it is beyond the scope of this text and the equation for collisional frequency of A and B is the following:

$$Z_{AB} = N_A N_B (r_A + r_B)^2 \sqrt{\frac{8\pi k_B T}{\mu_{AB}}} \tag{18.5.1}$$

with

- N_A and N_B are the numbers of A and B molecules in the system, respectively
- r_a and r_b are the radii of molecule A and B, respectively
- k_B is the Boltzmann constant k_B = 1.380 x 10^{-23} Joules Kelvin
- T is the temperature in Kelvin
- μ_{AB} is calculated via $\mu_{AB} = \frac{m_A m_B}{m_A + m_B}$

The specifics of Equation 18.5.1 are not important for this conversation, but it is important to identify that Z_{AB} increases with increasing density (i.e., increasing N_A and N_B), with increasing reactant size (r_a and r_b), with increasing velocities (predicted via Kinetic Molecular Theory), and with increasing temperature (although weakly because of the square root function).

A Video Discussing Collision Theory of Kinetics: Collusion Theory of Kinetics (opens in new window) [youtu.be]

Microscopic Factor 2: Activation Energy

Previously, we discussed the kinetic molecular theory of gases, which showed that the average kinetic energy of the particles of a gas increases with increasing temperature. Because the speed of a particle is proportional to the square root of its kinetic energy, increasing the temperature will also increase the number of collisions between molecules per unit time. What the kinetic molecular theory of gases does not explain is why the reaction rate of most reactions approximately doubles with a 10°C temperature increase. This result is surprisingly large considering that a 10°C increase in the temperature of a gas from 300 K to 310 K increases the kinetic energy of the particles by only about 4%, leading to an increase in molecular speed of only about 2% and a correspondingly small increase in the number of bimolecular collisions per unit time.

The collision model of chemical kinetics explains this behavior by introducing the concept of **activation energy** (E_a). We will define this concept using the reaction of NO with ozone, which plays an important role in the depletion of ozone in the ozone layer:

$$\mathrm{NO(g)+O_3(g)\rightarrow NO_2(g)+O_2(g)}$$

Increasing the temperature from 200 K to 350 K causes the rate constant for this particular reaction to increase by a factor of more than 10, whereas the increase in the frequency of bimolecular collisions over this temperature range is only 30%. Thus something other than an increase in the collision rate must be affecting the reaction rate.

Experimental rate law for this reaction is

$$\text{rate} = k[\mathrm{NO}][\mathrm{O_3}]$$

and is used to identify how the reaction rate (not the rate constant) vares with concentration. The rate constant, however, does vary with temperature. Figure $18.5.1$ shows a plot of the rate constant of the reaction of NO with O_3 at various temperatures. The relationship is not linear but instead resembles the relationships seen in graphs of vapor pressure versus temperature (e.g, the Clausius-Claperyon equation). In all three cases, the shape of the plots results from a distribution of kinetic energy over a population of particles (electrons in the case of conductivity; molecules in the case of vapor pressure; and molecules, atoms, or ions in the case of reaction rates). Only a fraction of the particles have sufficient energy to overcome an energy barrier.

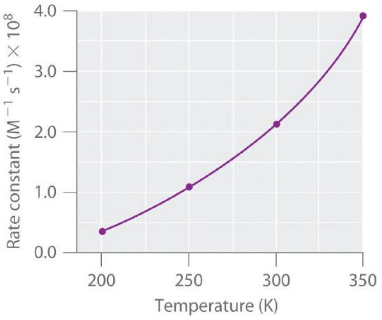


Figure 18.5.1: Rate Constant versus Temperature for the Reaction of NO with O_3The nonlinear shape of the curve is caused by a distribution of kinetic energy over a population of molecules. Only a fraction of the particles have enough energy to overcome an energy barrier, but as the temperature is increased, the size of that fraction increases. (CC BY-SA-NC; anonymous)

In the case of vapor pressure, particles must overcome an energy barrier to escape from the liquid phase to the gas phase. This barrier corresponds to the energy of the intermolecular forces that hold the molecules together in the liquid. In conductivity, the barrier is the energy gap between the filled and empty bands. In chemical reactions, the energy barrier corresponds to the amount of energy the particles must have to react when they collide. This energy threshold, called the **activation energy**, was first postulated in 1888 by the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry 1903). It is the minimum amount of energy needed for a reaction to occur. Reacting molecules must have enough energy to overcome electrostatic repulsion, and a minimum amount of energy is required to break chemical bonds so that new ones may be formed. Molecules that collide with less than the threshold energy bounce off one another chemically unchanged, with only their direction of travel and their speed altered by the collision. Molecules that are able to overcome the energy barrier are able to react and form an arrangement of atoms called the **activated complex** or the **transition state** of the reaction. The activated complex is not a reaction intermediate; it does not last long enough to be detected readily.

> *Any phenomenon that depends on the distribution of thermal energy in a population of particles has a nonlinear temperature dependence.*

We can graph the energy of a reaction by plotting the potential energy of the system as the reaction progresses. Figure 18.5.2shows a plot for the NO–O_3 system, in which the vertical axis is potential energy and the horizontal axis is the reaction coordinate, which indicates the progress of the reaction with time. The activated complex is shown in brackets with an asterisk. The overall change in potential energy for the reaction (ΔE) is negative, which means that the reaction releases energy. (In this case, ΔE is −200.8 kJ/mol.) To react, however, the molecules must overcome the energy barrier to reaction (E_a is 9.6 kJ/mol). That is, 9.6 kJ/mol must be put into the system as the activation energy. Below this threshold, the particles do not have enough energy for the reaction to occur.

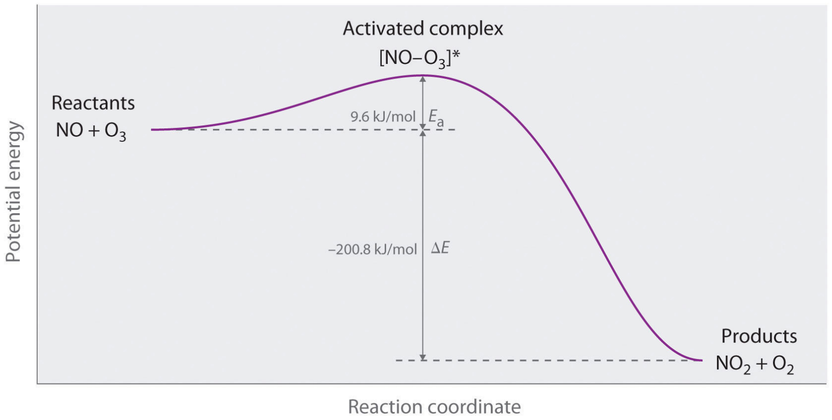


Figure 18.5.2: Energy of the Activated Complex for the NO–O_3 System. The diagram shows how the energy of this system varies as the reaction proceeds from reactants to products. Note the initial increase in energy required to form the activated complex. (CC BY-SA-NC; anonymous)

Figure 18.5.3a illustrates the general situation in which the products have a lower potential energy than the reactants. In contrast, Figure 18.5.3b illustrates the case in which the products have a higher potential energy than the reactants, so the overall reaction requires an input of energy; that is, it is energetically uphill, and \($\Delta E > 0$\). Although the energy changes that result from a reaction can be positive, negative, or even zero, in most cases an energy barrier must be overcome before a reaction can occur. This means that the activation energy is almost always positive; there is a class of reactions called barrierless reactions, but those are discussed elsewhere.

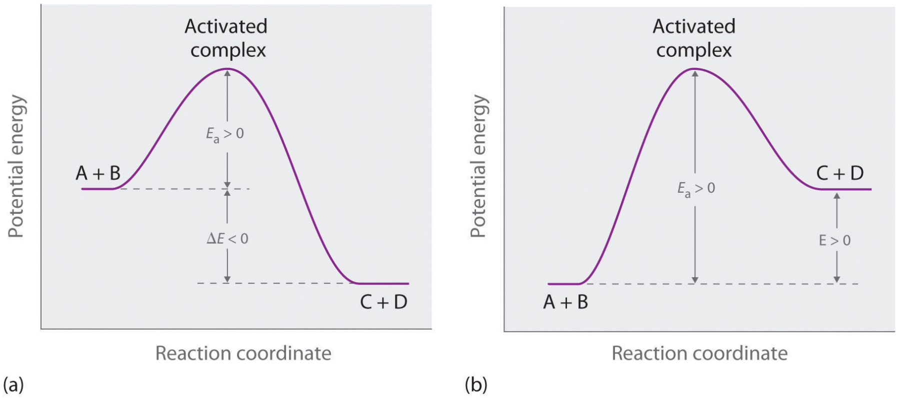


Figure 18.5.3: Differentiating between E_a and ΔE. The potential energy diagrams for a reaction with (a) $\Delta E < 0$ and (b) $\Delta E > 0$ illustrate the change in the potential energy of the system as reactants are converted to products. In both cases, E_a is positive. For a reaction such as the one shown in (b), E_a must be greater than ΔE. (CC BY-SA-NC; anonymous)

> *For similar reactions under comparable conditions, the one with the smallest E_a will occur most rapidly.*

Whereas ΔE is related to the tendency of a reaction to occur spontaneously, E_a gives us information about the reaction rate and how rapidly the reaction rate changes with temperature. For two similar reactions under comparable conditions, the reaction with the smallest E_a will occur more rapidly.

Figure 18.5.4 shows both the kinetic energy distributions and a potential energy diagram for a reaction. The shaded areas show that at the lower temperature (300 K), only a small fraction of molecules collide with kinetic energy greater than E_a; however, at the higher temperature (500 K) a much larger fraction of molecules collide with kinetic energy greater than E_a. Consequently, the reaction rate is much slower at the lower temperature because only a relatively few molecules collide with enough energy to overcome the potential energy barrier.

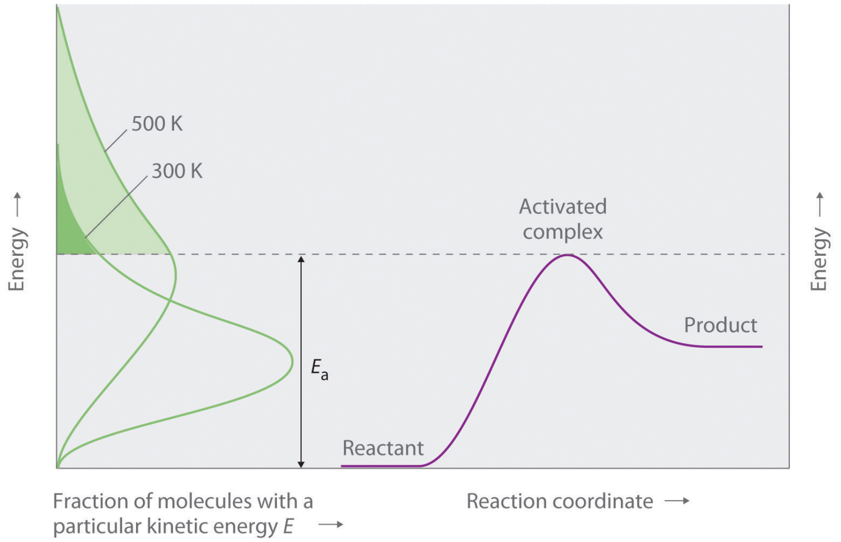


Figure 18.5.4: Surmounting the Energy Barrier to a Reaction. This chart juxtaposes the energy distributions of lower-temperature (300 K) and higher-temperature (500 K) samples of a gas against the potential energy diagram for a reaction. Only those molecules in the shaded region of the energy distribution curve have E > E_a and are therefore able to cross the energy barrier separating reactants and products. The fraction of molecules with $E > E_a$ is much greater at 500 K than at 300 K, so the reaction will occur much more rapidly at 500 K. (CC BY-SA-NC; anonymous)

Energy is on the y axis while reaction coordinate and fraction of molecules with a particular kinetic energy E are on the x axis.

Video Discussing Transition State Theory: Transition State Theory(opens in new window) [youtu.be]

Microscopic Factor 3: Sterics

Even when the energy of collisions between two reactant species is greater than E_a, most collisions do not produce a reaction. The probability of a reaction occurring depends not only on the collision energy but also on the spatial orientation of the molecules when they collide. For NO and O_3 to produce NO_2 and O_2, a terminal oxygen atom of O_3 must collide with the nitrogen atom of NO at an angle that allows O_3 to transfer an oxygen atom to NO to produce NO_2 (Figure 18.5.4). All other collisions produce no reaction. Because fewer than 1% of all possible orientations of NO and O_3 result in a reaction at kinetic energies greater than E_a, most collisions of NO and O_3 are unproductive. The fraction of orientations that result in a reaction is called the **steric factor** (ρ) and its value can range from $\rho = 0$ (no orientations of molecules result in reaction) to $\rho = 1$ (all orientations result in reaction).

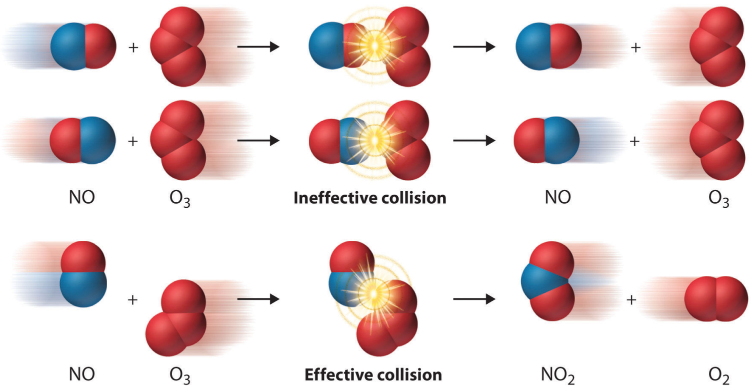


Figure 18.5.4: The Effect of Molecular Orientation on the Reaction of NO and O_3. Most collisions of NO and O_3 molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the terminal O atoms of O_3 are likely to produce NO_2 and O_2, even if the molecules collide with $E > E_a$. (CC BY-SA-NC; anonymous)

Macroscopic Behavior: The Arrhenius Equation

The collision model explains why most collisions between molecules do not result in a chemical reaction. For example, nitrogen and oxygen molecules in a single liter of air at room temperature and 1 atm of pressure collide about 10^{30} times per second. If every collision produced two molecules of NO, the atmosphere would have been converted to NO and then NO_2 a long time ago. Instead, in most collisions, the molecules simply bounce off one another without reacting, much as marbles bounce off each other when they collide.

For an $A + B$ elementary reaction, all three microscopic factors discussed above that affect the reaction rate can be summarized in a single relationship:

$$\text{rate} = (\text{collision frequency}) \times (\text{steric factor}) \times (\text{fraction of collisions with } E > E_a)$$

where

$$\text{rate} = k[A][B] \tag{18.5.2}$$

Arrhenius used these relationships to arrive at an equation that relates the magnitude of the rate constant for a reaction to the temperature, the activation energy, and the constant, A, called the **frequency factor**:

$$k = Ae^{-E_a/RT} \tag{18.5.3}$$

The frequency factor is used to convert concentrations to collisions per second (scaled by the steric factor). Because the frequency of collisions depends on the temperature, A is actually not constant (Equation 18.5.1). Instead, A increases slightly with temperature as the increased kinetic energy of molecules at higher temperatures causes them to move slightly faster and thus undergo more collisions per unit time.

Equation 18.5.3 is known as the **Arrhenius equation** and summarizes the collision model of chemical kinetics, where T is the absolute temperature (in K) and R is the ideal gas constant [8.314 J/(K·mol)]. E_a indicates the sensitivity of the reaction to changes in temperature. The reaction rate with a large E_a increases rapidly with increasing temperature, whereas the reaction rate with a smaller E_a increases much more slowly with increasing temperature.

If we know the reaction rate at various temperatures, we can use the Arrhenius equation to calculate the activation energy. Taking the natural logarithm of both sides of Equation 18.5.3,

$$\ln k = \ln A + \left(-\frac{E_\mathrm{a}}{RT}\right) \tag{18.5.4}$$

$$= \ln A + \left[\left(-\frac{E_\mathrm{a}}{R}\right)\left(\frac{1}{T}\right)\right] \tag{18.5.5}$$

Equation 18.5.5 is the equation of a straight line,

$$y = mx + b$$

where $y = \ln k$ and $x = 1/T$. This means that a plot of $\ln k$ versus $1/T$ is a straight line with a slope of $-E_a/R$ and an intercept of $\ln A$. In fact, we need to measure the reaction rate at only two temperatures to estimate E_a.

Knowing the E_a at one temperature allows us to predict the reaction rate at other temperatures. This is important in cooking and food preservation, for example, as well as in controlling industrial reactions to prevent potential disasters. The procedure for determining E_a from reaction rates measured at several temperatures is illustrated in Example $18.5.1$.

A Video Discussing The Arrhenius Equation: The Arrhenius Equation(opens in new window) [youtu.be]

✓ Example 18.5.1: Chirping Tree Crickets

Many people believe that the rate of a tree cricket's chirping is related to temperature. To see whether this is true, biologists have carried out accurate measurements of the rate of tree cricket chirping (f) as a function of temperature (T). Use the data in the following table, along with the graph of ln[chirping rate] versus $1/T$ to calculate E_a for the biochemical reaction that controls cricket chirping. Then predict the chirping rate on a very hot evening, when the temperature is 308 K (35°C, or 95°F).

Chirping Tree Crickets Frequency Table

Frequency (f; chirps/min)	ln f	T (K)	1/T (K)
200	5.30	299	3.34×10^{-3}
179	5.19	298	3.36×10^{-3}
158	5.06	296	3.38×10^{-3}
141	4.95	294	3.40×10^{-3}
126	4.84	293	3.41×10^{-3}
112	4.72	292	3.42×10^{-3}
100	4.61	290	3.45×10^{-3}
89	4.49	289	3.46×10^{-3}
79	4.37	287	3.48×10^{-3}

Given: chirping rate at various temperatures

Asked for: activation energy and chirping rate at specified temperature

Strategy:

A. From the plot of $\ln f$ versus $1/T$, calculate the slope of the line ($-E_a/R$) and then solve for the activation energy.
B. Express Equation 18.5.5 in terms of k_1 and T_1 and then in terms of k_2 and T_2.
C. Subtract the two equations; rearrange the result to describe k_2/k_1 in terms of T_2 and T_1.

D. Using measured data from the table, solve the equation to obtain the ratio k_2/k_1. Using the value listed in the table for k_1, solve for k_2.

Solution

A If cricket chirping is controlled by a reaction that obeys the Arrhenius equation, then a plot of $\ln f$ versus $1/T$ should give a straight line (Figure 18.5.6).

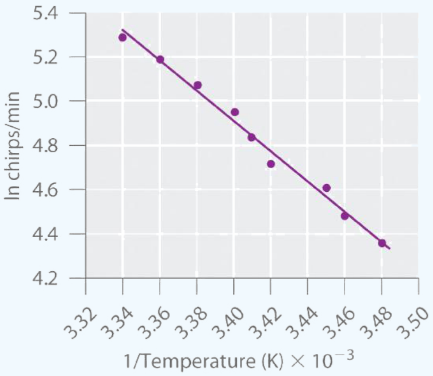


Figure 18.5.6: Graphical Determination of E_a for Tree Cricket Chirping. When the natural logarithm of the rate of tree cricket chirping is plotted versus 1/T, a straight line results. The slope of the line suggests that the chirping rate is controlled by a single reaction with an E_a of 55 kJ/mol. (CC BY-SA-NC; anonymous)

Also, the slope of the plot of $\ln f$ versus $1/T$ should be equal to $-E_a/R$. We can use the two endpoints in Figure 18.5.6 to estimate the slope:

$$\begin{aligned}\text{slope} &= \frac{\Delta \ln f}{\Delta(1/T)} \\ &= \frac{5.30 - 4.37}{3.34 \times 10^{-3}\ \text{K}^{-1} - 3.48 \times 10^{-3}\ \text{K}^{-1}} \\ &= \frac{0.93}{-0.14 \times 10^{-3}\ \text{K}^{-1}} \\ &= -6.6 \times 10^{3}\ \text{K}\end{aligned}$$

A computer best-fit line through all the points has a slope of -6.67×10^3 K, so our estimate is very close. We now use it to solve for the activation energy:

$$\begin{aligned}E_\text{a} &= -(\text{slope})(R) \\ &= -(-6.6 \times 10^3\ \text{K})\left(\frac{8.314\ \text{J}}{\text{K} \cdot \text{mol}}\right)\left(\frac{1\ \text{KJ}}{1000\ \text{J}}\right) \\ &= \frac{55\ \text{kJ}}{\text{mol}}\end{aligned}$$

B If the activation energy of a reaction and the rate constant at one temperature are known, then we can calculate the reaction rate at any other temperature. We can use Equation 18.5.5 to express the known rate constant (k_1) at the first temperature (T_1) as follows:

$$\ln k_1 = \ln A - \frac{E_\text{a}}{RT_1}$$

Similarly, we can express the unknown rate constant (k_2) at the second temperature (T_2) as follows:

$$\ln k_2 = \ln A - \frac{E_\text{a}}{RT_2}$$

C These two equations contain four known quantities (E_a, T_1, T_2, and k_1) and two unknowns (A and k_2). We can eliminate A by subtracting the first equation from the second:

$$\begin{aligned}\ln k_2-\ln k_1 &= \left(\ln A-\frac{E_a}{RT_2}\right)-\left(\ln A-\frac{E_a}{RT_1}\right)\\ &= -\frac{E_a}{RT_2}+\frac{E_a}{RT_1}\end{aligned}$$

Then

$$\ln\frac{k_2}{k_1}=\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

D To obtain the best prediction of chirping rate at 308 K (T_2), we try to choose for T_1 and k_1 the measured rate constant and corresponding temperature in the data table that is closest to the best-fit line in the graph. Choosing data for T_1 = 296 K, where f = 158, and using the E_a calculated previously,

$$\begin{aligned}\ln\frac{k_{T_2}}{k_{T_1}} &= \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\\ &= \frac{55\text{ kJ/mol}}{8.314\text{ J/(K}\cdot\text{mol)}}\left(\frac{1000\text{ J}}{1\text{ kJ}}\right)\left(\frac{1}{296\text{ K}}-\frac{1}{308\text{ K}}\right)\\ &= 0.87\end{aligned}$$

Thus k_{308}/k_{296} = 2.4 and k_{308} = (2.4)(158) = 380, and the chirping rate on a night when the temperature is 308 K is predicted to be 380 chirps per minute.

? Exercise 18.5.1A

The equation for the decomposition of NO_2 to NO and O_2 is second order in NO_2:

$$2\,NO_2(g)\rightarrow 2\,NO(g)+O_2(g)$$

Data for the reaction rate as a function of temperature are listed in the following table. Calculate E_a for the reaction and the rate constant at 700 K.

Data for the reaction rate as a function of temperature

T (K)	k ($M^{-1}\cdot s^{-1}$)
592	522
603	755
627	1700
652	4020
656	5030

Answer

E_a = 114 kJ/mol; k_{700}= 18,600 $M^{-1}\cdot s^{-1}$ = 1.86 × 10^4 $M^{-1}\cdot s^{-1}$.

? Exercise 18.5.1B

What E_a results in a doubling of the reaction rate with a 10°C increase in temperature from 20° to 30°C?

Answer

about 51 kJ/mol

A Video Discussing Graphing Using the Arrhenius Equation: Graphing Using the Arrhenius Equation (opens in new window) [youtu.be] (opens in new window)

Summary

For a chemical reaction to occur, an energy threshold must be overcome, and the reacting species must also have the correct spatial orientation. The Arrhenius equation is $k=Ae^{-E_a/RT}$. A minimum energy (activation energy,vE_a) is required for a collision between molecules to result in a chemical reaction. Plots of potential energy for a system versus the reaction coordinate show an energy barrier that must be overcome for the reaction to occur. The arrangement of atoms at the highest point of this barrier is the activated complex, or transition state, of the reaction. At a given temperature, the higher the E_a, the slower the reaction. The fraction of orientations that result in a reaction is the steric factor. The frequency factor, steric factor, and activation energy are related to the rate constant in the Arrhenius equation: $k=Ae^{-E_a/RT}$. A plot of the natural logarithm of k versus $1/T$ is a straight line with a slope of $-E_a/R$.

18.6: A Deeper Look: Reaction Dynamics

under construction

18.7: Kinetics of Catalysis

Learning Objectives

- To understand how catalysts increase the reaction rate and the selectivity of chemical reactions.

Catalysts are substances that increase the reaction rate of a chemical reaction without being consumed in the process. A catalyst, therefore, does not appear in the overall stoichiometry of the reaction it catalyzes, but it must appear in at least one of the elementary reactions in the mechanism for the catalyzed reaction. The catalyzed pathway has a lower E_a, but the net change in energy that results from the reaction (the difference between the energy of the reactants and the energy of the products) is not affected by the presence of a catalyst (Figure 18.7.1). Nevertheless, because of its lower E_a, the reaction rate of a catalyzed reaction is faster than the reaction rate of the uncatalyzed reaction at the same temperature. Because a catalyst decreases the height of the energy barrier, its presence increases the reaction rates of both the forward and the reverse reactions by the same amount. In this section, we will examine the three major classes of catalysts: heterogeneous catalysts, homogeneous catalysts, and enzymes.

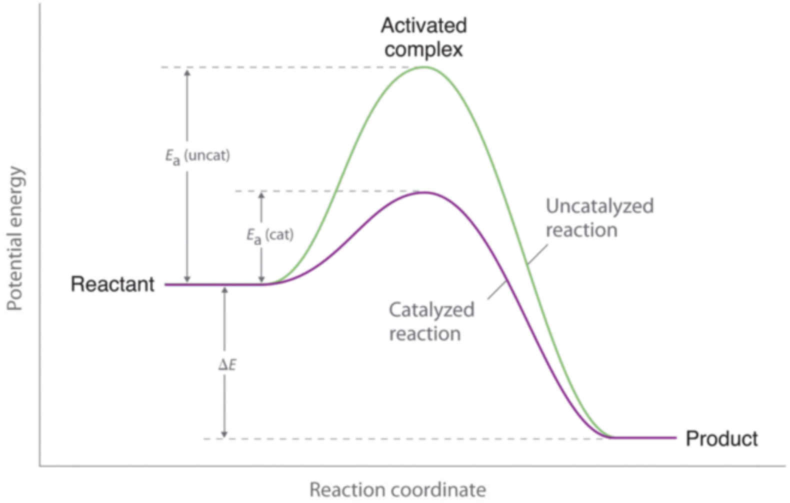


Figure 18.7.1: Lowering the Activation Energy of a Reaction by a Catalyst. This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect the energy of the reactants or products (and thus does not affect ΔE). (CC BY-NC-SA; anonymous)

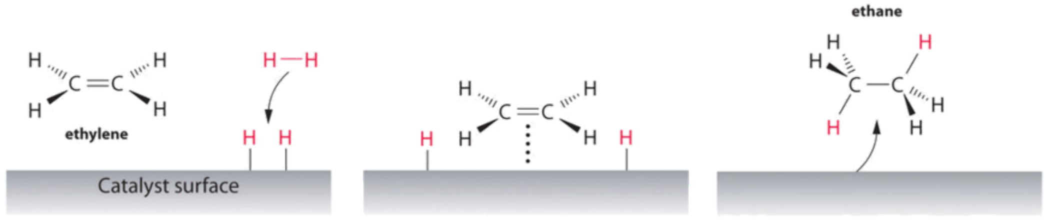
The green line represents the uncatalyzed reaction. The purple line represent the catalyzed reaction .

> *A catalyst affects E_a, not ΔE.*

Heterogeneous Catalysis

In **heterogeneous catalysis**, the catalyst is in a different phase from the reactants. At least one of the reactants interacts with the solid surface in a physical process called adsorption in such a way that a chemical bond in the reactant becomes weak and then breaks. Poisons are substances that bind irreversibly to catalysts, preventing reactants from adsorbing and thus reducing or destroying the catalyst's efficiency.

An example of heterogeneous catalysis is the interaction of hydrogen gas with the surface of a metal, such as Ni, Pd, or Pt. As shown in part (a) in Figure 18.7.2, the hydrogen–hydrogen bonds break and produce individual adsorbed hydrogen atoms on the surface of the metal. Because the adsorbed atoms can move around on the surface, two hydrogen atoms can collide and form a molecule of hydrogen gas that can then leave the surface in the reverse process, called desorption. Adsorbed H atoms on a metal surface are substantially more reactive than a hydrogen molecule. Because the relatively strong H–H bond (dissociation energy = 432 kJ/mol) has already been broken, the energy barrier for most reactions of H_2 is substantially lower on the catalyst surface.



(a) Hydrogen (H_2) adsorbs to the catalyst surface (M) to form adsorbed H atoms.

(b) Ethylene (C_2H_4) adsorbs to the catalyst surface.

(c) Ethylene reacts with adsorbed H atoms to give the product ethane (C_2H_6).

Figure 18.7.2: Hydrogenation of Ethylene on a Heterogeneous Catalyst. When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H_2. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released. (CC BY-NC-SA; anonymous)

Figure $18.7.2$ shows a process called *hydrogenation*, in which hydrogen atoms are added to the double bond of an alkene, such as ethylene, to give a product that contains C–C single bonds, in this case ethane. Hydrogenation is used in the food industry to convert vegetable oils, which consist of long chains of alkenes, to more commercially valuable solid derivatives that contain alkyl chains. Hydrogenation of some of the double bonds in polyunsaturated vegetable oils, for example, produces margarine, a product with a melting point, texture, and other physical properties similar to those of butter.

Several important examples of industrial heterogeneous catalytic reactions are in Table $18.7.1$. Although the mechanisms of these reactions are considerably more complex than the simple hydrogenation reaction described here, they all involve adsorption of the reactants onto a solid catalytic surface, chemical reaction of the adsorbed species (sometimes via a number of intermediate species), and finally desorption of the products from the surface.

Table 18.7.1: Some Commercially Important Reactions that Employ Heterogeneous Catalysts

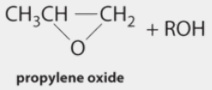
Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
contact process	V_2O_5 or Pt	$2SO_2 + O_2 \rightarrow 2SO_3$	H_2SO_4
Haber process	Fe, K_2O, Al_2O_3	$N_2 + 3H_2 \rightarrow 2NH_3$	NH_3
Ostwald process	Pt and Rh	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	HNO_3
water–gas shift reaction	Fe, Cr_2O_3, or Cu	$CO + H_2O \rightarrow CO_2 + H_2$	H_2 for NH_3, CH_3OH, and other fuels
steam reforming	Ni	$CH_4 + H_2O \rightarrow CO + 3H_2$	H_2
methanol synthesis	ZnO and Cr_2O_3	$CO + 2H_2 \rightarrow CH_3OH$	CH_3OH
Sohio process	bismuth phosphomolybdate	$CH_2{=}CHCH_3 + NH_3 + \frac{3}{2}O_2 \rightarrow \underset{\text{acrylonitrile}}{CH_2{=}CHCN} + 3H_2O$	$CH_2{=}CHCN$
catalytic hydrogenation	Ni, Pd, or Pt	$RCH{=}CHR' + H2 \rightarrow RCH_2—CH_2R'$	partially hydrogenated oils for margarine, and so forth

Homogeneous Catalysis

In **homogeneous catalysis**, the catalyst is in the same phase as the reactant(s). The number of collisions between reactants and catalyst is at a maximum because the catalyst is uniformly dispersed throughout the reaction mixture. Many homogeneous catalysts in industry are transition metal compounds (Table $18.7.2$), but recovering these expensive catalysts from solution has been a major challenge. As an added barrier to their widespread commercial use, many homogeneous catalysts can be used only at relatively low temperatures, and even then they tend to decompose slowly in solution. Despite these problems, a number of commercially viable processes have been developed in recent years. High-density polyethylene and polypropylene are produced by homogeneous catalysis.

Table 18.7.2: Some Commercially Important Reactions that Employ Homogeneous Catalysts

Commercial Process	Catalyst	Reactants	Final Product

Commercial Process	Catalyst	Reactants	Final Product
Union Carbide	$[Rh(CO)_2I_2]^-$	$CO + CH_3OH$	CH_3CO_2H
hydroperoxide process	Mo(VI) complexes	$CH_3CH{=}CH_2$ + R–O–O–H	
hydroformylation	Rh/PR_3 complexes	$RCH{=}CH_2 + CO + H_2$	RCH_2CH_2CHO
adiponitrile process	Ni/PR_3complexes	$2HCN + CH_2{=}CHCH{=}CH_2$	$NCCH_2CH_2CH_2CH_2CN$ used to synthesize nylon
olefin polymerization	$(RC_5H_5)_2ZrCl_2$	$CH_2{=}CH_2$	$–(CH_2CH_2–)_n$: high-density polyethylene

Enzymes

Enzymes, catalysts that occur naturally in living organisms, are almost all protein molecules with typical molecular masses of 20,000–100,000 amu. Some are homogeneous catalysts that react in aqueous solution within a cellular compartment of an organism. Others are heterogeneous catalysts embedded within the membranes that separate cells and cellular compartments from their surroundings. The reactant in an enzyme-catalyzed reaction is called a **substrate**.

Because enzymes can increase reaction rates by enormous factors (up to 10^{17} times the uncatalyzed rate) and tend to be very specific, typically producing only a single product in quantitative yield, they are the focus of active research. At the same time, enzymes are usually expensive to obtain, they often cease functioning at temperatures greater than 37 °C, have limited stability in solution, and have such high specificity that they are confined to turning one particular set of reactants into one particular product. This means that separate processes using different enzymes must be developed for chemically similar reactions, which is time-consuming and expensive. Thus far, enzymes have found only limited industrial applications, although they are used as ingredients in laundry detergents, contact lens cleaners, and meat tenderizers. The enzymes in these applications tend to be proteases, which are able to cleave the amide bonds that hold amino acids together in proteins. Meat tenderizers, for example, contain a protease called papain, which is isolated from papaya juice. It cleaves some of the long, fibrous protein molecules that make inexpensive cuts of beef tough, producing a piece of meat that is more tender. Some insects, like the bombadier beetle, carry an enzyme capable of catalyzing the decomposition of hydrogen peroxide to water (Figure $18.7.3$).

Figure 18.7.3: A Catalytic Defense Mechanism. The scalding, foul-smelling spray emitted by this bombardier beetle is produced by the catalytic decomposition of H_2O_2.

Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of an enzyme and thus slowing or preventing a reaction from occurring. Irreversible inhibitors are therefore the equivalent of poisons in heterogeneous catalysis. One of the oldest and most widely used commercial enzyme inhibitors is aspirin, which selectively inhibits one of the enzymes involved in the synthesis of molecules that trigger inflammation. The design and synthesis of related molecules that are more effective, more selective, and less toxic than aspirin are important objectives of biomedical research.

Summary

Catalysts participate in a chemical reaction and increase its rate. They do not appear in the reaction's net equation and are not consumed during the reaction. Catalysts allow a reaction to proceed via a pathway that has a lower activation energy than the uncatalyzed reaction. In heterogeneous catalysis, catalysts provide a surface to which reactants bind in a process of adsorption. In homogeneous catalysis, catalysts are in the same phase as the reactants. Enzymes are biological catalysts that produce large increases in reaction rates and tend to be specific for certain reactants and products. The reactant in an enzyme-catalyzed reaction is called a substrate. Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction.

CHAPTER OVERVIEW

19: Nuclear Chemistry

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

Template:HideTOC

Until now, you have studied chemical processes in which atoms share or transfer electrons to form new compounds, leaving the atomic nuclei largely unaffected. In this chapter, we examine some properties of the atomic nucleus and the changes that can occur in atomic nuclei. Nuclear reactions differ from other chemical processes in one critical way: in a nuclear reaction, **the identities of the elements change**. In addition, nuclear reactions are often accompanied by the release of enormous amounts of energy, as much as a *billion* times more than the energy released by chemical reactions. Moreover, the yields and rates of a nuclear reaction are generally unaffected by changes in temperature, pressure, or the presence of a catalyst.

We begin by examining the structure of the atomic nucleus and the factors that determine whether a particular nucleus is stable or decays spontaneously to another element. We then discuss the major kinds of nuclear decay reactions, as well as the properties and uses of the radiation emitted when nuclei decay. You will learn how radioactive emissions can be used to study the mechanisms of chemical reactions and biological processes and how to calculate the amount of energy released during a nuclear reaction. You will also discover why houses are tested for radon gas, how radiation is used to probe organs such as the brain, and how the energy from nuclear reactions can be harnessed to produce electricity. Last, we explore the nuclear chemistry that takes place in stars, and we describe the role that stars play in producing most of the elements in the universe.

19.1: Mass-Energy Relationships in Nuclei

Learning Objectives

- To understand the factors that affect nuclear stability.

Although most of the known elements have at least one isotope whose atomic nucleus is stable indefinitely, all elements have isotopes that are unstable and disintegrate, or decay, at measurable rates by emitting radiation. Some elements have no stable isotopes and eventually decay to other elements. In contrast to the chemical reactions that were the main focus of earlier chapters and are due to changes in the arrangements of the valence electrons of atoms, the process of nuclear decay results in changes inside an atomic nucleus. We begin our discussion of nuclear reactions by reviewing the conventions used to describe the components of the nucleus.

The Atomic Nucleus

Each element can be represented by the notation $^{A}_{Z}\text{X}$, where *A*, the mass number, is the sum of the number of protons and the number of neutrons, and *Z*, the atomic number, is the number of protons. The protons and neutrons that make up the nucleus of an atom are called **nucleons**, and an atom with a particular number of protons and neutrons is called a **nuclide**. Nuclides with the same number of protons but different numbers of neutrons are called **isotopes**. Isotopes can also be represented by an alternative notation that uses the name of the element followed by the mass number, such as carbon-12. The stable isotopes of oxygen, for example, can be represented in any of the following ways:

stable isotopes of oxygen represented in different ways

$^{A}_{Z}\text{X}$	$^{16}_{8}\text{O}$	$^{17}_{8}\text{O}$	$^{18}_{8}\text{O}$
^{A}X	^{16}O	^{17}O	^{18}O
element-A:	oxygen-16	oxygen-17	oxygen-18

Because the number of neutrons is equal to $A - Z$, we see that the first isotope of oxygen has 8 neutrons, the second isotope 9 neutrons, and the third isotope 10 neutrons. Isotopes of all naturally occurring elements on Earth are present in nearly fixed proportions, with each proportion constituting an isotope's *natural abundance*. For example, in a typical terrestrial sample of oxygen, 99.76% of the O atoms is oxygen-16, 0.20% is oxygen-18, and 0.04% is oxygen-17. Any nucleus that is unstable and decays spontaneously is said to be **radioactive**, emitting subatomic particles and electromagnetic radiation. The emissions are collectively called *radioactivity* and can be measured. Isotopes that emit radiation are called **radioisotopes**.

Nuclear Stability

The nucleus of an atom occupies a tiny fraction of the volume of an atom and contains the number of protons and neutrons that is characteristic of a given isotope. Electrostatic repulsions would normally cause the positively charged protons to repel each other, but the nucleus does not fly apart because of the **strong nuclear force**, an extremely powerful but very short-range attractive force between nucleons (Figure 19.1.1). All stable nuclei except the hydrogen-1 nucleus (^{1}H) contain at least one neutron to overcome the electrostatic repulsion between protons. As the number of protons in the nucleus increases, the number of neutrons needed for a stable nucleus increases even more rapidly. Too many protons (or too few neutrons) in the nucleus result in an imbalance between forces, which leads to nuclear instability.

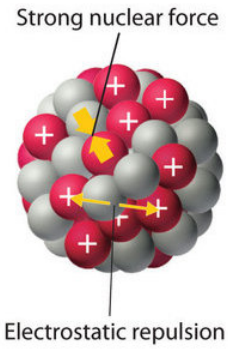


Figure 19.1.1: Competing Interactions within the Atomic Nucleus. Electrostatic repulsions between positively charged protons would normally cause the nuclei of atoms (except H) to fly apart. In stable atomic nuclei, these repulsions are overcome by the strong nuclear force, a short-range but powerful attractive interaction between nucleons. If the attractive interactions due to the strong nuclear force are weaker than the electrostatic repulsions between protons, the nucleus is unstable, and it will eventually decay.

The relationship between the number of protons and the number of neutrons in stable nuclei, arbitrarily defined as having a half-life longer than 10 times the age of Earth, is shown graphically in Figure $19.1.2$. The stable isotopes form a “peninsula of stability” in a “sea of instability.” Only two stable isotopes, ^1H and ^3He, have a neutron-to-proton ratio less than 1. Several stable isotopes of light atoms have a neutron-to-proton ratio equal to 1 (e.g., ^4_2He, $^{10}_5B$, and $^{40}_{20}Ca$). All other stable nuclei have a higher neutron-to-proton ratio, which increases steadily to about 1.5 for the heaviest nuclei. Regardless of the number of neutrons, however, all elements with Z > 83 are unstable and radioactive.

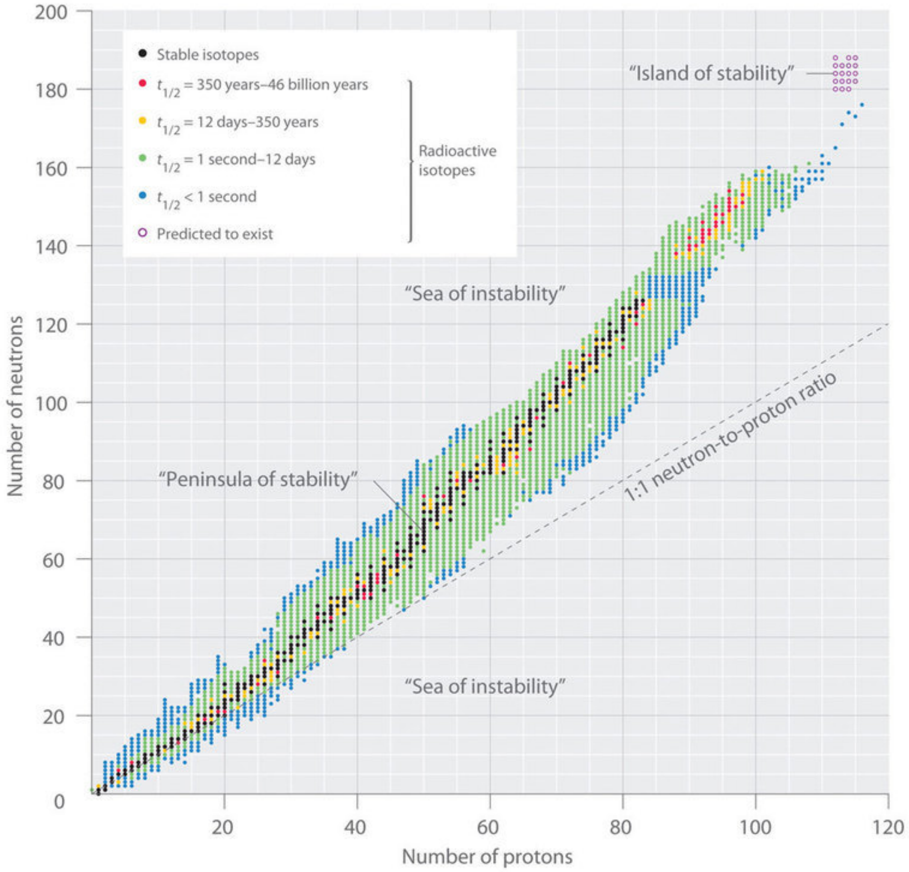


Figure 19.1.2: The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio. In this plot of the number of neutrons versus the number of protons, each black point corresponds to a stable nucleus. In this classification, a stable nucleus is arbitrarily defined as one with a half-life longer than 46 billion years (10 times the age of Earth). As the number of protons (the atomic number) increases, the number of neutrons required for a stable nucleus increases even more rapidly. Isotopes shown in red, yellow, green, and blue are progressively less stable and more radioactive; the farther an isotope is from the diagonal band of stable isotopes, the shorter its half-life. The purple dots indicate superheavy nuclei that are predicted to be relatively stable, meaning that they are expected to be radioactive but to have relatively long half-lives. In most cases, these elements have not yet been observed or synthesized. Data source: National Nuclear Data Center, Brookhaven National Laboratory, Evaluated Nuclear Structure Data File (ENSDF), Chart of Nuclides, http://www.nndc.bnl.gov/chart.

Graph of number or neutrons against the number or protons. The graph is divided into sections of "sea of instability", "peninsula of stability", "sea of instability" and "island of stability"

As shown in Figure 19.1.3, more than half of the stable nuclei (166 out of 279) have *even* numbers of both neutrons and protons; only 6 of the 279 stable nuclei do not have odd numbers of both. Moreover, certain numbers of neutrons or protons result in especially stable nuclei; these are the so-called *magic numbers* 2, 8, 20, 50, 82, and 126. For example, tin (Z = 50) has 10 stable isotopes, but the elements on either side of tin in the periodic table, indium (Z = 49) and antimony (Z = 51), have only 2 stable isotopes each. Nuclei with magic numbers of *both* protons *and* neutrons are said to be "doubly magic" and are even more stable. Examples of elements with doubly magic nuclei are $^{4}_{2}\text{He}$, with 2 protons and 2 neutrons, and $^{208}_{82}\text{Pb}$, with 82 protons and 126 neutrons, which is the heaviest known stable isotope of any element.

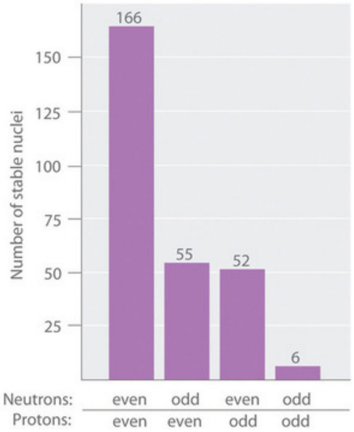


Figure 19.1.3: The Relationship between the Number of Protons and the Number of Neutrons and Nuclear Stability.

> *Most stable nuclei contain* ***even*** *numbers of both neutrons and protons*

The pattern of stability suggested by the magic numbers of nucleons is reminiscent of the stability associated with the closed-shell electron configurations of the noble gases in group 18 and has led to the hypothesis that the nucleus contains shells of nucleons that are in some ways analogous to the shells occupied by electrons in an atom. As shown in Figure 19.1.2, the "peninsula" of stable isotopes is surrounded by a "reef" of radioactive isotopes, which are stable enough to exist for varying lengths of time before they eventually decay to produce other nuclei.

Origin of the Magic Numbers

Multiple models have been formulated to explain the origin of the magic numbers and two popular ones are the Nuclear Shell Model and the Liquid Drop Model. Unfortuneatly, both require advanced quantum mechanics to fully understand and are beyond the scope of this text.

✓ Example 19.1.1

Classify each nuclide as stable or radioactive.

a. $^{30}_{15}\text{P}$
b. $^{98}_{43}\text{Tc}$
c. tin-118
d. $^{239}_{94}\text{Pu}$

Given: mass number and atomic number

Asked for: predicted nuclear stability

Strategy:

Use the number of protons, the neutron-to-proton ratio, and the presence of even or odd numbers of neutrons and protons to predict the stability or radioactivity of each nuclide.

Solution:

a. This isotope of phosphorus has 15 neutrons and 15 protons, giving a neutron-to-proton ratio of 1.0. Although the atomic number, 15, is much less than the value of 83 above which all nuclides are unstable, the neutron-to-proton ratio is less than that expected for stability for an element with this mass. As shown in Figure 19.1.2, its neutron-to-proton ratio should be greater than 1. Moreover, this isotope has an odd number of both neutrons and protons, which also tends to make a nuclide unstable. Consequently, $^{30}_{15}\text{P}$ is predicted to be radioactive, and it is.

b. This isotope of technetium has 55 neutrons and 43 protons, giving a neutron-to-proton ratio of 1.28, which places $^{98}_{43}\text{Tc}$ near the edge of the band of stability. The atomic number, 55, is much less than the value of 83 above which all isotopes are unstable. These facts suggest that $^{98}_{43}\text{Tc}$ might be stable. However, $^{98}_{43}\text{Tc}$ has an odd number of both neutrons and protons, a combination that seldom gives a stable nucleus. Consequently, $^{98}_{43}\text{Tc}$ is predicted to be radioactive, and it is.

c. Tin-118 has 68 neutrons and 50 protons, for a neutron-to-proton ratio of 1.36. As in part b, this value and the atomic number both suggest stability. In addition, the isotope has an even number of both neutrons and protons, which tends to increase nuclear stability. Most important, the nucleus has 50 protons, and 50 is one of the magic numbers associated with especially stable nuclei. Thus $^{118}_{50}\mathrm{Sn}$should be particularly stable.

d. This nuclide has an atomic number of 94. Because all nuclei with Z > 83 are unstable, $^{239}_{94}\mathrm{Pu}$ must be radioactive.

? Exercise 19.1.1

Classify each nuclide as stable or radioactive.

a. $^{232}_{90}\mathrm{Th}$
b. $^{40}_{20}\mathrm{Ca}$
c. $^{15}_{8}\mathrm{O}$
d. $^{139}_{57}\mathrm{La}$

Answer a

radioactive

Answer b

stable

Answer c

radioactive

Answer d

stable

Superheavy Elements

In addition to the “peninsula of stability” there is a small “island of stability” that is predicted to exist in the upper right corner. This island corresponds to the **superheavy elements**, with atomic numbers near the magic number 126. Because the next magic number for neutrons should be 184, it was suggested that an element with 114 protons and 184 neutrons might be stable enough to exist in nature. Although these claims were met with skepticism for many years, since 1999 a few atoms of isotopes with $Z = 114$ and $Z = 116$ have been prepared and found to be surprisingly stable. One isotope of element 114 lasts 2.7 seconds before decaying, described as an “eternity” by nuclear chemists. Moreover, there is recent evidence for the existence of a nucleus with $A = 292$ that was found in $^{232}\mathrm{Th}$. With an estimated half-life greater than 10^8 years, the isotope is particularly stable. Its measured mass is consistent with predictions for the mass of an isotope with $Z = 122$. Thus a number of relatively long-lived nuclei may well be accessible among the superheavy elements.

Summary

Subatomic particles of the nucleus (protons and neutrons) are called **nucleons**. A **nuclide** is an atom with a particular number of protons and neutrons. An unstable nucleus that decays spontaneously is **radioactive**, and its emissions are collectively called *radioactivity*. Isotopes that emit radiation are called **radioisotopes**. Each nucleon is attracted to other nucleons by the **strong nuclear force**. Stable nuclei generally have even numbers of both protons and neutrons and a neutron-to-proton ratio of at least 1. Nuclei that contain *magic numbers* of protons and neutrons are often especially stable. **Superheavy elements**, with atomic numbers near 126, may even be stable enough to exist in nature.

19.2: Nuclear Decay Processes

Learning Objectives

- To understand how nuclear transmutation reactions lead to the formation of the elements in stars and how they can be used to synthesize transuranium elements.

The relative abundances of the elements in the known universe vary by more than 12 orders of magnitude. For the most part, these differences in abundance cannot be explained by differences in nuclear stability. Although the ^{56}Fe nucleus is the most stable nucleus known, the most abundant element in the known universe is not iron, but hydrogen (^{1}H), which accounts for about 90% of all atoms. In fact, ^{1}H is the raw material from which all other elements are formed. In this section, we explain why ^{1}H and ^{2}He together account for at least 99% of all the atoms in the known universe. We also describe the nuclear reactions that take place in stars, which transform one nucleus into another and create all the naturally occurring elements.

Relative Abundances of the Elements on Earth and in the Known Universe

The relative abundances of the elements in the known universe and on Earth relative to silicon are shown in Figure $19.2.1$. The data are estimates based on the characteristic emission spectra of the elements in stars, the absorption spectra of matter in clouds of interstellar dust, and the approximate composition of Earth as measured by geologists. The data in Figure $19.2.1$ illustrate two important points. First, except for hydrogen, the most abundant elements have even atomic numbers. Not only is this consistent with the known trends in nuclear stability, but it also suggests that heavier elements are formed by combining helium nuclei (Z = 2). Second, the relative abundances of the elements in the known universe and on Earth are often very different, as indicated by the data in Table $19.2.1$ for some common elements.

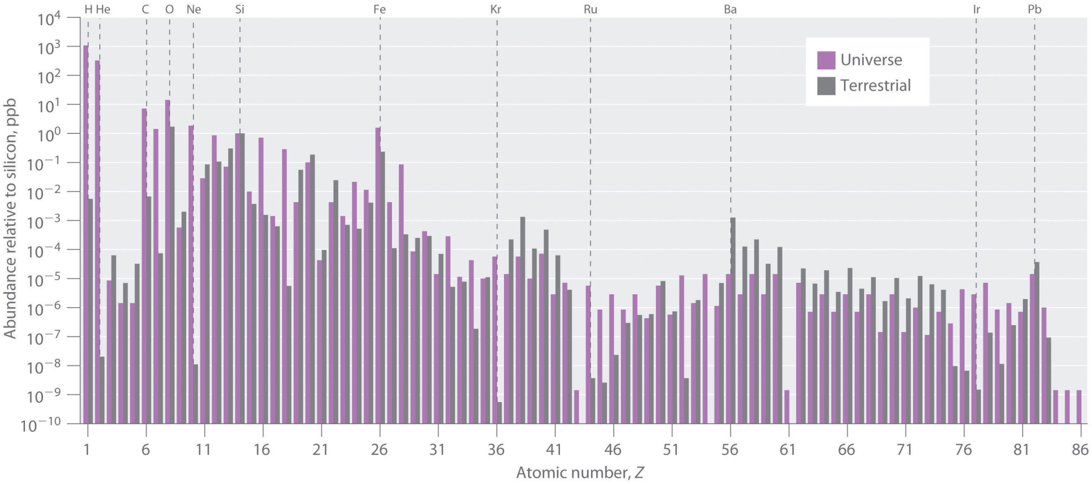


Figure 19.2.1: The Relative Abundances of the Elements in the Universe and on Earth. In this logarithmic plot, the relative abundances of the elements relative to that of silicon (arbitrarily set equal to 1) in the universe (green bars) and on Earth (purple bars) are shown as a function of atomic number. Elements with even atomic numbers are generally more abundant in the universe than elements with odd atomic numbers. Also, the relative abundances of many elements in the universe are very different from their relative abundances on Earth. (CC BY-NC-SA 3.0; anonymous)

Bar graph of abundance realtive to silicon in pbb against atomic number. The purple bars are universe elements while the gray bars are terrestrial elements.

Some of these differences are easily explained. For example, nonmetals such as H, He, C, N, O, Ne, and Kr are much less abundant relative to silicon on Earth than they are in the rest of the universe. These elements are either noble gases (He, Ne, and Kr) or elements that form volatile hydrides, such as NH_3, CH_4, and H_2O. Because Earth’s gravity is not strong enough to hold such light substances in the atmosphere, these elements have been slowly diffusing into outer space ever since our planet was formed. Argon is an exception; it is relatively abundant on Earth compared with the other noble gases because it is continuously produced in rocks by the radioactive decay of isotopes such as ^{40}K. In contrast, many metals, such as Al, Na, Fe, Ca, Mg, K, and Ti, are relatively abundant on Earth because they form nonvolatile compounds, such as oxides, that cannot escape into space. Other metals, however, are much less abundant on Earth than in the universe; some examples are Ru and Ir. This section explains some of the reasons for the great differences in abundances of the metallic elements.

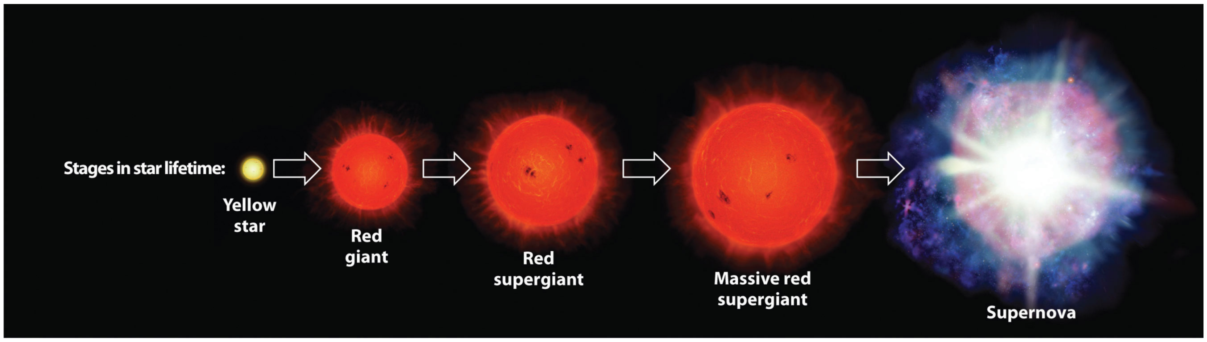
Table 19.2.1: Relative Abundances of Elements on Earth and in the Known Universe

Terrestrial/Universal Element	Abundance Ratio
H	0.0020
He	2.4×10^{-8}
C	0.36
N	0.02
O	46
Ne	1.9×10^{-6}
Na	1200
Mg	48
Al	1600
Si	390
S	0.84
K	5000
Ca	710
Ti	2200
Fe	57

All the elements originally present on Earth (and on other planets) were synthesized from hydrogen and helium nuclei in the interiors of stars that have long since exploded and disappeared. Six of the most abundant elements in the universe (C, O, Ne, Mg, Si, and Fe) have nuclei that are integral multiples of the helium-4 nucleus, which suggests that helium-4 is the primary building block for heavier nuclei.

Synthesis of the Elements in Stars

Elements are synthesized in discrete stages during the lifetime of a star, and some steps occur only in the most massive stars known (Figure $19.2.2$). Initially, all stars are formed by the aggregation of interstellar "dust," which is mostly hydrogen. As the cloud of dust slowly contracts due to gravitational attraction, its density eventually reaches about 100 g/cm^3, and the temperature increases to about 1.5×10^7 K, forming a dense plasma of ionized hydrogen nuclei. At this point, self-sustaining nuclear reactions begin, and the star "ignites," creating a yellow star like our sun.



Core Temperature:	1.5×10^7 K	2×10^8 K	7×10^8 K	3×10^9 K	1×10^{11} K
Primary Nuclear Reaction:	^{1}H fusion	^{4}He fusion	^{4}He + ^{12}C ^{12}C + ^{12}C ^{12}C + ^{16}O	Proton–neutron exchange reactions	Multiple neutron captures
Elements Formed:	He	C, O, Ne, Mg	Na, Si, S, Ar, Ca	Fe, Ni	Elements with $Z > 28$

Figure 19.2.2: Nuclear Reactions during the Life Cycle of a Massive Star. At each stage in the lifetime of a star, a different fuel is used for nuclear fusion, resulting in the formation of different elements. Fusion of hydrogen to give helium is the primary fusion reaction in young stars. As the star ages, helium accumulates and begins to "burn," undergoing fusion to form heavier elements such as carbon and oxygen. As the adolescent star matures, significant amounts of iron and nickel are formed by fusion of the heavier elements formed previously. The heaviest elements are formed only during the final death throes of the star—the formation of a nova or supernova.

The stages in a stare lifetime are yellow star, red giant, red supergiant, massive red supergiant and finally supernova.

In the first stage of its life, the star is powered by a series of nuclear fusion reactions that convert hydrogen to helium:

$$\begin{aligned} {}^{1}_{1}\mathrm{H} + {}^{1}_{1}\mathrm{H} &\rightarrow {}^{2}_{1}\mathrm{H} + {}^{0}_{+1}\beta \\ {}^{2}_{1}\mathrm{H} + {}^{1}_{1}\mathrm{H} &\rightarrow {}^{3}_{2}\mathrm{He} + {}^{0}_{0}\gamma \\ {}^{3}_{2}\mathrm{He} + {}^{3}_{2}\mathrm{He} &\rightarrow {}^{4}_{2}\mathrm{He} + 2{}^{1}_{1}\mathrm{H} \end{aligned} \tag{19.2.1}$$

The overall reaction is the conversion of four hydrogen nuclei to a helium-4 nucleus, which is accompanied by the release of two positrons, two γ rays, and a great deal of energy:

$$4{}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + 2{}^{0}_{+1}\beta + 2{}^{0}_{0}\gamma \tag{19.2.2}$$

These reactions are responsible for most of the enormous amount of energy that is released as sunlight and solar heat. It takes several billion years, depending on the size of the star, to convert about 10% of the hydrogen to helium.

Once large amounts of helium-4 have been formed, they become concentrated in the core of the star, which slowly becomes denser and hotter. At a temperature of about 2 × 10^8 K, the helium-4 nuclei begin to fuse, producing beryllium-8:

$$2{}^{4}_{2}\mathrm{He} \rightarrow {}^{8}_{4}\mathrm{Be} \tag{19.2.3}$$

Although beryllium-8 has both an even mass number and an even atomic number, its also has a low neutron-to-proton ratio (and other factors beyond the scope of this text) that makes it unstable; it decomposes in only about 10^{-16} s. Nonetheless, this is long enough for it to react with a third helium-4 nucleus to form carbon-12, which is very stable. Sequential reactions of carbon-12 with helium-4 produce the elements with even numbers of protons and neutrons up to magnesium-24:

$${}^{8}_{4}\mathrm{Be} \xrightarrow{{}^{4}_{2}\mathrm{He}} {}^{12}_{6}\mathrm{C} \xrightarrow{{}^{4}_{2}\mathrm{He}} {}^{16}_{8}\mathrm{O} \xrightarrow{{}^{4}_{2}\mathrm{He}} {}^{20}_{10}\mathrm{Ne} \xrightarrow{{}^{4}_{2}\mathrm{He}} {}^{24}_{12}\mathrm{Mg} \tag{19.2.4}$$

So much energy is released by these reactions that it causes the surrounding mass of hydrogen to expand, producing a red giant that is about 100 times larger than the original yellow star.

As the star expands, heavier nuclei accumulate in its core, which contracts further to a density of about 50,000 g/cm3, so the core becomes even hotter. At a temperature of about 7 × 10^8 K, carbon and oxygen nuclei undergo nuclear fusion reactions to produce sodium and silicon nuclei:

$${}^{12}_{6}\mathrm{C} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{23}_{11}\mathrm{Na} + {}^{1}_{1}\mathrm{H} \tag{19.2.5}$$

$${}^{12}_{6}\mathrm{C} + {}^{16}_{8}\mathrm{O} \rightarrow {}^{28}_{14}\mathrm{Si} + {}^{0}_{0}\gamma \tag{19.2.6}$$

At these temperatures, carbon-12 reacts with helium-4 to initiate a series of reactions that produce more oxygen-16, neon-20, magnesium-24, and silicon-28, as well as heavier nuclides such as sulfur-32, argon-36, and calcium-40:

$$^{12}_{6}\text{C} \xrightarrow{^{4}_{2}\text{He}} {}^{16}_{8}\text{O} \xrightarrow{^{4}_{2}\text{He}} {}^{20}_{10}\text{Ne} \xrightarrow{^{4}_{2}\text{He}} {}^{24}_{12}\text{Mg} \xrightarrow{^{4}_{2}\text{He}} {}^{28}_{14}\text{Si} \xrightarrow{^{4}_{2}\text{He}} {}^{32}_{16}\text{S} \xrightarrow{^{4}_{2}\text{He}} {}^{36}_{18}\text{Ar} \xrightarrow{^{4}_{2}\text{He}} {}^{40}_{20}\text{Ca} \tag{19.2.7}$$

The energy released by these reactions causes a further expansion of the star to form a red supergiant, and the core temperature increases steadily. At a temperature of about 3 × 10^9 K, the nuclei that have been formed exchange protons and neutrons freely. This equilibration process forms heavier elements up to iron-56 and nickel-58, which have the most stable nuclei known.

The Formation of Heavier Elements in Supernovas

None of the processes described so far produces nuclei with $Z > 28$. All naturally occurring elements heavier than nickel are formed in the rare but spectacular cataclysmic explosions called supernovas (Figure 19.2.2). When the fuel in the core of a very massive star has been consumed, its gravity causes it to collapse in about 1 s. As the core is compressed, the iron and nickel nuclei within it disintegrate to protons and neutrons, and many of the protons capture electrons to form neutrons. The resulting neutron star is a dark object that is so dense that atoms no longer exist. Simultaneously, the energy released by the collapse of the core causes the supernova to explode in what is arguably the single most violent event in the universe. The force of the explosion blows most of the star’s matter into space, creating a gigantic and rapidly expanding dust cloud, or nebula (Figure 19.2.3). During the extraordinarily short duration of this event, the concentration of neutrons is so great that multiple neutron-capture events occur, leading to the production of the heaviest elements and many of the less stable nuclides. Under these conditions, for example, an iron-56 nucleus can absorb as many as 64 neutrons, briefly forming an extraordinarily unstable iron isotope that can then undergo multiple rapid β-decay processes to produce tin-120:

$$^{56}_{26}\text{Fe} + 64^{1}_{0}\text{n} \rightarrow {}^{120}_{26}\text{Fe} \rightarrow {}^{120}_{50}\text{Sn} + 24^{0}_{-1}\beta \tag{19.2.8}$$

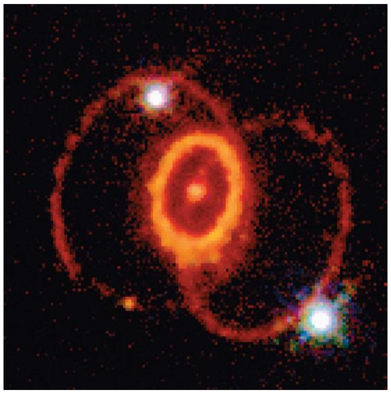


Figure 19.2.3: A Supernova. A view of the remains of Supernova 1987A, located in the Large Magellanic Cloud, showing the circular halo of expanding debris produced by the explosion. Multiple neutron-capture events occur during a supernova explosion, forming both the heaviest elements and many of the less stable nuclides.

Although a supernova occurs only every few hundred years in a galaxy such as the Milky Way, these rare explosions provide the only conditions under which elements heavier than nickel can be formed. The force of the explosions distributes these elements throughout the galaxy surrounding the supernova, and eventually they are captured in the dust that condenses to form new stars. Based on its elemental composition, our sun is thought to be a second- or third-generation star. It contains a considerable amount of cosmic debris from the explosion of supernovas in the remote past.

✓ Example 19.2.1: Carbon Burning Stars

The reaction of two carbon-12 nuclei in a carbon-burning star can produce elements other than sodium. Write a balanced nuclear equation for the formation of

a. magnesium-24.
b. neon-20 from two carbon-12 nuclei.

Given: reactant and product nuclides

Asked for: balanced nuclear equation

Strategy:

Use conservation of mass and charge to determine the type of nuclear reaction that will convert the reactant to the indicated product. Write the balanced nuclear equation for the reaction.

Solution

a. A magnesium-24 nucleus (Z = 12, A = 24) has the same nucleons as two carbon-12 nuclei (Z = 6, A = 12). The reaction is therefore a fusion of two carbon-12 nuclei, and no other particles are produced: ${}^{12}_{6}\mathrm{C} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{24}_{12}\mathrm{Mg}$.
b. The neon-20 product has Z = 10 and A = 20. The conservation of mass requires that the other product have A = (2 × 12) − 20 = 4; because of conservation of charge, it must have Z = (2 × 6) − 10 = 2. These are the characteristics of an α particle. The reaction is therefore ${}^{12}_{6}\mathrm{C} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{20}_{10}\mathrm{Ne} + {}^{4}_{2}\alpha$.

? Exercise 19.2.1

How many neutrons must an iron-56 nucleus absorb during a supernova explosion to produce an arsenic-75 nucleus? Write a balanced nuclear equation for the reaction.

Answer

19 neutrons; ${}^{56}_{26}\mathrm{Fe} + 19{}^{1}_{0}\mathrm{n} \rightarrow {}^{75}_{26}\mathrm{Fe} \rightarrow {}^{75}_{33}\mathrm{As} + 7{}^{0}_{-1}\beta$

Summary

Hydrogen and helium are the most abundant elements in the universe. Heavier elements are formed in the interior of stars via multiple neutron-capture events. By far the most abundant element in the universe is hydrogen. The fusion of hydrogen nuclei to form helium nuclei is the major process that fuels young stars such as the sun. Elements heavier than helium are formed from hydrogen and helium in the interiors of stars. Successive fusion reactions of helium nuclei at higher temperatures create elements with even numbers of protons and neutrons up to magnesium and then up to calcium. Eventually, the elements up to iron-56 and nickel-58 are formed by exchange processes at even higher temperatures. Heavier elements can only be made by a process that involves multiple neutron-capture events, which can occur only during the explosion of a supernova.

19.3: Kinetics of Radioactive Decay

Learning Objectives

- To know how to use half-lives to describe the rates of first-order reactions

Another approach to describing reaction rates is based on the time required for the concentration of a reactant to decrease to one-half its initial value. This period of time is called the **half-life** of the reaction, written as $t_{1/2}$. Thus the half-life of a reaction is the time required for the reactant concentration to decrease from $[A]_0$ to $[A]_{0/2}$. If two reactions have the same order, the faster reaction will have a shorter half-life, and the slower reaction will have a longer half-life.

The half-life of a first-order reaction under a given set of reaction conditions is a constant. This is not true for zeroth- and second-order reactions. The half-life of a first-order reaction is independent of the concentration of the reactants. This becomes evident when we rearrange the integrated rate law for a first-order reaction to produce the following equation:

$$\ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]} = kt \tag{19.3.1}$$

Substituting $[A]_{0/2}$ for $[A]$ and $t_{1/2}$ for t (to indicate a half-life) into Equation 19.3.1 gives

$$\ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]_0/2} = \ln 2 = kt_{1/2} \tag{19.3.2}$$

Substituting $\ln 2 \approx 0.693$ into the equation results in the expression for the half-life of a first-order reaction:

$$t_{1/2} = \frac{0.693}{k} \tag{19.3.3}$$

Thus, for a first-order reaction, each successive half-life is the same length of time, as shown in Figure $19.3.1$, and is *independent* of [A].

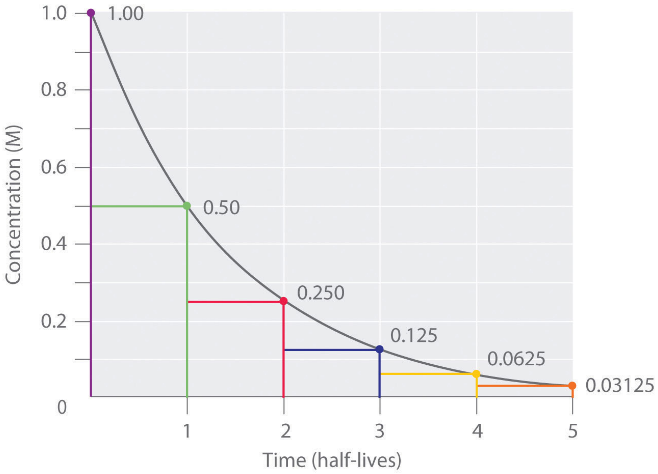


Figure 19.3.1: The Half-Life of a First-Order Reaction. This plot shows the concentration of the reactant in a first-order reaction as a function of time and identifies a series of half-lives, intervals in which the reactant concentration decreases by a factor of 2. In a first-order reaction, every half-life is the same length of time.

If we know the rate constant for a first-order reaction, then we can use half-lives to predict how much time is needed for the reaction to reach a certain percent completion.

Number of Half-Lives	Percentage of Reactant Remaining	
1	$\frac{100\%}{2} = 50\%$	$\frac{1}{2}(100\%) = 50\%$
2	$\frac{50\%}{2} = 25\%$	$\frac{1}{2}\left(\frac{1}{2}\right)(100\%) = 25\%$

Number of Half-Lives	Percentage of Reactant Remaining	
3	$\frac{25\%}{2} = 12.5\%$	$\frac{1}{2}\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)(100\%) = 12.5\%$
n	$\frac{100\%}{2^n}$	$\left(\frac{1}{2}\right)^n(100\%) = \left(\frac{1}{2}\right)^n\%$

As you can see from this table, the amount of reactant left after n half-lives of a first-order reaction is $(1/2)^n$ times the initial concentration.

> *For a first-order reaction, the concentration of the reactant decreases by a constant with each half-life and is independent of [A].*

✓ Example 19.3.1

The anticancer drug cis-platin hydrolyzes in water with a rate constant of 1.5×10^{-3} min^{-1} at pH 7.0 and 25°C. Calculate the half-life for the hydrolysis reaction under these conditions. If a freshly prepared solution of cis-platin has a concentration of 0.053 M, what will be the concentration of cis-platin after 5 half-lives? after 10 half-lives? What is the percent completion of the reaction after 5 half-lives? after 10 half-lives?

Given: rate constant, initial concentration, and number of half-lives

Asked for: half-life, final concentrations, and percent completion

Strategy:

A. Use Equation 19.3.3 to calculate the half-life of the reaction.
B. Multiply the initial concentration by 1/2 to the power corresponding to the number of half-lives to obtain the remaining concentrations after those half-lives.
C. Subtract the remaining concentration from the initial concentration. Then divide by the initial concentration, multiplying the fraction by 100 to obtain the percent completion.

Solution

A We can calculate the half-life of the reaction using Equation 19.3.3:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-3}\ \text{min}^{-1}} = 4.6 \times 10^2\ \text{min}$$

Thus it takes almost 8 h for half of the cis-platin to hydrolyze.

B After 5 half-lives (about 38 h), the remaining concentration of cis-platin will be as follows:

$$\frac{0.053\ \text{M}}{2^5} = \frac{0.053\ \text{M}}{32} = 0.0017\ \text{M}$$

After 10 half-lives (77 h), the remaining concentration of cis-platin will be as follows:

$$\frac{0.053\ \text{M}}{2^{10}} = \frac{0.053\ \text{M}}{1024} = 5.2 \times 10^{-5}\ \text{M}$$

C The percent completion after 5 half-lives will be as follows:

$$\text{percent completion} = \frac{(0.053\ \text{M} - 0.0017\ \text{M})(100)}{0.053} = 97\%$$

The percent completion after 10 half-lives will be as follows:

$$\text{percent completion} = \frac{(0.053\ \text{M} - 5.2 \times 10^{-5}\ \text{M})(100)}{0.053\ \text{M}} = 100\%$$

Thus a first-order chemical reaction is 97% complete after 5 half-lives and 100% complete after 10 half-lives.

Exercise 19.3.1

Ethyl chloride decomposes to ethylene and HCl in a first-order reaction that has a rate constant of $1.6 \times 10^{-6}\ s^{-1}$ at 650°C.

a. What is the half-life for the reaction under these conditions?
b. If a flask that originally contains 0.077 M ethyl chloride is heated at 650°C, what is the concentration of ethyl chloride after 4 half-lives?

Answer a

4.3×10^{5} s = 120 h = 5.0 days;

Answer b

4.8×10^{-3} M

Radioactive Decay Rates

Radioactivity, or radioactive decay, is the emission of a particle or a photon that results from the spontaneous decomposition of the unstable nucleus of an atom. The rate of radioactive decay is an intrinsic property of each radioactive isotope that is independent of the chemical and physical form of the radioactive isotope. The rate is also independent of temperature. In this section, we will describe radioactive decay rates and how half-lives can be used to monitor radioactive decay processes.

In any sample of a given radioactive substance, the number of atoms of the radioactive isotope must decrease with time as their nuclei decay to nuclei of a more stable isotope. Using N to represent the number of atoms of the radioactive isotope, we can define the **rate of decay** of the sample, which is also called its **activity (*A*)** as the decrease in the number of the radioisotope’s nuclei per unit time:

$$A = -\frac{\Delta N}{\Delta t} \tag{19.3.4}$$

Activity is usually measured in disintegrations per second (dps) or disintegrations per minute (dpm).

The activity of a sample is directly proportional to the number of atoms of the radioactive isotope in the sample:

$$A = kN \tag{19.3.5}$$

Here, the symbol k is the radioactive decay constant, which has units of inverse time (e.g., s^{-1}, yr^{-1}) and a characteristic value for each radioactive isotope. If we combine Equation 19.3.4 and Equation 19.3.5, we obtain the relationship between the number of decays per unit time and the number of atoms of the isotope in a sample:

$$-\frac{\Delta N}{\Delta t} = kN \tag{19.3.6}$$

Equation 19.3.6 is the same as the equation for the reaction rate of a first-order reaction, except that it uses numbers of atoms instead of concentrations. In fact, radioactive decay is a first-order process and can be described in terms of either the differential rate law (Equation 19.3.6) or the integrated rate law:

$$N = N_0 e^{-kt} \tag{19.3.7}$$

$$\ln \frac{N}{N_0} = -kt \tag{19.3.8}$$

Because radioactive decay is a first-order process, the time required for half of the nuclei in any sample of a radioactive isotope to decay is a constant, called the half-life of the isotope. The half-life tells us how radioactive an isotope is (the number of decays per unit time); thus it is the most commonly cited property of any radioisotope. For a given number of atoms, isotopes with shorter half-lives decay more rapidly, undergoing a greater number of radioactive decays per unit time than do isotopes with longer half-lives. The half-lives of several isotopes are listed in Table 14.6, along with some of their applications.

Table 19.3.2: Half-Lives and Applications of Some Radioactive Isotopes

Radioactive Isotope	Half-Life	Typical Uses
*The *m* denotes metastable, where an excited state nucleus decays to the ground state of the same isotope.		

Radioactive Isotope	Half-Life	Typical Uses
hydrogen-3 (tritium)	12.32 yr	biochemical tracer
carbon-11	20.33 min	positron emission tomography (biomedical imaging)
carbon-14	5.70×10^3 yr	dating of artifacts
sodium-24	14.951 h	cardiovascular system tracer
phosphorus-32	14.26 days	biochemical tracer
potassium-40	1.248×10^9 yr	dating of rocks
iron-59	44.495 days	red blood cell lifetime tracer
cobalt-60	5.2712 yr	radiation therapy for cancer
technetium-99*m**	6.006 h	biomedical imaging
iodine-131	8.0207 days	thyroid studies tracer
radium-226	1.600×10^3 yr	radiation therapy for cancer
uranium-238	4.468×10^9 yr	dating of rocks and Earth’s crust
americium-241	432.2 yr	smoke detectors

*The *m* denotes metastable, where an excited state nucleus decays to the ground state of the same isotope.

Note

Radioactive decay is a first-order process.

Radioisotope Dating Techniques

In our earlier discussion, we used the half-life of a first-order reaction to calculate how long the reaction had been occurring. Because nuclear decay reactions follow first-order kinetics and have a rate constant that is independent of temperature and the chemical or physical environment, we can perform similar calculations using the half-lives of isotopes to estimate the ages of geological and archaeological artifacts. The techniques that have been developed for this application are known as radioisotope dating techniques.

The most common method for measuring the age of ancient objects is carbon-14 dating. The carbon-14 isotope, created continuously in the upper regions of Earth’s atmosphere, reacts with atmospheric oxygen or ozone to form $^{14}CO_2$. As a result, the CO_2 that plants use as a carbon source for synthesizing organic compounds always includes a certain proportion of $^{14}CO_2$ molecules as well as nonradioactive $^{12}CO_2$ and $^{13}CO_2$. Any animal that eats a plant ingests a mixture of organic compounds that contains approximately the same proportions of carbon isotopes as those in the atmosphere. When the animal or plant dies, the carbon-14 nuclei in its tissues decay to nitrogen-14 nuclei by a radioactive process known as beta decay, which releases low-energy electrons (β particles) that can be detected and measured:

$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + \beta^- \tag{19.3.9}$$

The half-life for this reaction is 5700 ± 30 yr.

The $^{14}C/^{12}C$ ratio in living organisms is 1.3×10^{-12}, with a decay rate of 15 dpm/g of carbon (Figure $19.3.2$). Comparing the disintegrations per minute per gram of carbon from an archaeological sample with those from a recently living sample enables scientists to estimate the age of the artifact, as illustrated in Example 11.Using this method implicitly assumes that the $^{14}CO_2/^{12}CO_2$ ratio in the atmosphere is constant, which is not strictly correct. Other methods, such as tree-ring dating, have been used to calibrate the dates obtained by radiocarbon dating, and all radiocarbon dates reported are now corrected for minor changes in the $^{14}CO_2/^{12}CO_2$ ratio over time.

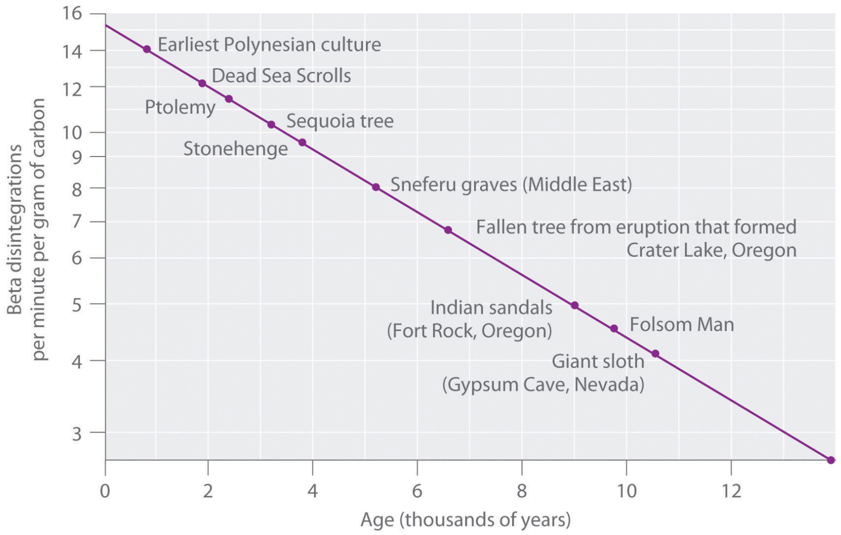


Figure 19.3.2: Radiocarbon Dating. A plot of the specific activity of ^{14}C versus age for a number of archaeological samples shows an inverse linear relationship between ^{14}C content (a log scale) and age (a linear scale).

✓ Example 19.3.2

In 1990, the remains of an apparently prehistoric man were found in a melting glacier in the Italian Alps. Analysis of the ^{14}C content of samples of wood from his tools gave a decay rate of 8.0 dpm/g carbon. How long ago did the man die?

Given: isotope and final activity

Asked for: elapsed time

Strategy:

A Use Equation 19.3.5 to calculate N_0/N. Then substitute the value for the half-life of ^{14}C into Equation 19.3.3 to find the rate constant for the reaction.

B Using the values obtained for N_0/N and the rate constant, solve Equation 19.3.8 to obtain the elapsed time.

Solution

We know the initial activity from the isotope's identity (15 dpm/g), the final activity (8.0 dpm/g), and the half-life, so we can use the integrated rate law for a first-order nuclear reaction (Equation 19.3.8) to calculate the elapsed time (the amount of time elapsed since the wood for the tools was cut and began to decay).

$$\ln \frac{N}{N_0} = -kt \tag{19.3.10}$$

$$\frac{\ln(N/N_0)}{k} = t \tag{19.3.11}$$

A From Equation 19.3.5, we know that $A = kN$. We can therefore use the initial and final activities (A_0 = 15 dpm and A = 8.0 dpm) to calculate N_0/N:

$$\frac{A_0}{A} = \frac{kN_0}{kN} = \frac{N_0}{N} = \frac{15}{8.0}$$

Now we need only calculate the rate constant for the reaction from its half-life (5730 yr) using Equation 19.3.3:

$$t_{1/2} = \frac{0.693}{k}$$

This equation can be rearranged as follows:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ yr}} = 1.22 \times 10^{-4} \text{ yr}^{-1}$$

B Substituting into the equation for *t*,

$$t = \frac{\ln(N_0/N)}{k} = \frac{\ln(15/8.0)}{1.22 \times 10^{-4} \text{ yr}^{-1}} = 5.2 \times 10^3 \text{ yr}$$

From our calculations, the man died 5200 yr ago.

Exercise 19.3.2

It is believed that humans first arrived in the Western Hemisphere during the last Ice Age, presumably by traveling over an exposed land bridge between Siberia and Alaska. Archaeologists have estimated that this occurred about 11,000 yr ago, but some argue that recent discoveries in several sites in North and South America suggest a much earlier arrival. Analysis of a sample of charcoal from a fire in one such site gave a ^{14}C decay rate of 0.4 dpm/g of carbon. What is the approximate age of the sample?

Answer

30,000 yr

Summary

- The half-life of a first-order reaction is independent of the concentration of the reactants.
- The half-lives of radioactive isotopes can be used to date objects.

The half-life of a reaction is the time required for the reactant concentration to decrease to one-half its initial value. The half-life of a first-order reaction is a constant that is related to the rate constant for the reaction: $t_{1/2} = 0.693/k$. Radioactive decay reactions are first-order reactions. The rate of decay, or activity, of a sample of a radioactive substance is the decrease in the number of radioactive nuclei per unit time.

19.4: Radiation in Biology and Medicine

Learning Objectives

- To know the differences between ionizing and nonionizing radiation and their effects on matter.
- To identify natural and artificial sources of radiation.

Because nuclear reactions do not typically affect the valence electrons of the atom (although electron capture draws an electron from an orbital of the lowest energy level), they do not directly cause chemical changes. Nonetheless, the particles and the photons emitted during nuclear decay are very energetic, and they can indirectly produce chemical changes in the matter surrounding the nucleus that has decayed. For instance, an α particle is an ionized helium nucleus (He^{2+}) that can act as a powerful oxidant. In this section, we describe how radiation interacts with matter and the some of the chemical and biological effects of radiation.

Ionizing versus Nonionizing Radiation

The effects of radiation on matter are determined primarily by the energy of the radiation, which depends on the nuclear decay reaction that produced it. **Nonionizing radiation** is relatively low in energy; when it collides with an atom in a molecule or an ion, most or all of its energy can be absorbed without causing a structural or a chemical change. Instead, the kinetic energy of the radiation is transferred to the atom or molecule with which it collides, causing it to rotate, vibrate, or move more rapidly. Because this energy can be transferred to adjacent molecules or ions in the form of heat, many radioactive substances are warm to the touch. Highly radioactive elements such as polonium, for example, have been used as heat sources in the US space program. As long as the intensity of the nonionizing radiation is not great enough to cause overheating, it is relatively harmless, and its effects can be neutralized by cooling.

In contrast, **ionizing radiation** is higher in energy, and some of its energy can be transferred to one or more atoms with which it collides as it passes through matter. If enough energy is transferred, electrons can be excited to very high energy levels, resulting in the formation of positively charged ions:

$$\text{atom} + \text{ionizing radiation} \rightarrow \text{ion}^+ + \text{e}^- \tag{19.4.1}$$

Molecules that have been ionized in this way are often highly reactive, and they can decompose or undergo other chemical changes that create a cascade of reactive molecules that can damage biological tissues and other materials (Figure 19.4.1). Because the energy of ionizing radiation is very high, we often report its energy in units such as megaelectronvolts (MeV) per particle:

$$1\ \text{MeV/particle} = 96\ \text{billion J/mol.}$$

Figure 19.4.1: Radiation Damage. When high-energy particles emitted by radioactive decay interact with matter, they can break bonds or ionize molecules, resulting in changes in physical properties such as ductility or color. The glass electrical insulator on the left has not been exposed to radiation, but the insulator on the right has received intense radiation doses over a long period of time. Radiation damage changed the chemical structure of the glass, causing it to become bright blue. (CC BY-SA-NC; anonymous)

The Effects of Ionizing Radiation on Matter

The effects of ionizing radiation depend on four factors:

1. The type of radiation, which dictates how far it can penetrate into matter
2. The energy of the individual particles or photons
3. The number of particles or photons that strike a given area per unit time
4. The chemical nature of the substance exposed to the radiation

The relative abilities of the various forms of ionizing radiation to penetrate biological tissues are illustrated in Figure 19.4.2. Because of its high charge and mass, α radiation interacts strongly with matter. Consequently, it does not penetrate deeply into an object, and it can be stopped by a piece of paper, clothing, or skin. In contrast, γ rays, with no charge and essentially no mass, do not interact strongly with matter and penetrate deeply into most objects, including the human body. Several inches of lead or more than 12 inches of special concrete are needed to completely stop γ rays. Because β particles are intermediate in mass and charge between α particles and γ rays, their interaction with matter is also intermediate. Beta particles readily penetrate paper or skin, but they can be stopped by a piece of wood or a relatively thin sheet of metal.

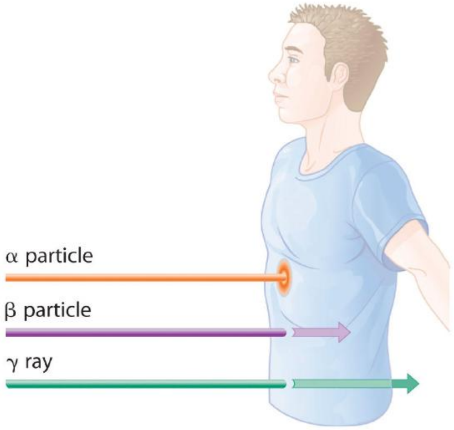


Figure 19.4.2: Depth of Penetration of Ionizing Radiation. The depth of penetration of alpha, beta, and gamma radiation varies with the particle. Because α particles interact strongly with matter, they do not penetrate deeply into the human body. In contrast, β particles do not interact as strongly with matter and penetrate more deeply. Gamma rays, which have no charge, are stopped by only very dense materials and can pass right through the human body without being absorbed. (CC BY-SA-NC; anonymous)

Because of their great penetrating ability, γ rays are by far the most dangerous type of radiation when they come from a source *outside* the body. Alpha particles, however, are the most damaging if their source is *inside* the body because internal tissues absorb all of their energy. Thus danger from radiation depends strongly on the type of radiation emitted and the extent of exposure, which allows scientists to safely handle many radioactive materials if they take precautions to avoid, for example, inhaling fine particulate dust that contains alpha emitters. Some properties of ionizing radiation are summarized in Table 19.4.1.

Table 19.4.1: Some Properties of Ionizing Radiation

Type	Energy Range (MeV)	Penetration Distance in Water*	Penetration Distance in Air*
α particles	3–9	< 0.05 mm	< 10 cm
β particles	≤ 3	< 4 mm	1 m
x-rays	$<10^{-2}$	< 1 cm	< 3 m
γ rays	10^{-2}–10^{1}	< 20 cm	> 3 m
*Distance at which half of the radiation has been absorbed.			

There are many different ways to measure radiation exposure, or the dose. The **roentgen (R)**, which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure.Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered x-rays. The roentgen is actually defined as the amount of radiation needed to produce an electrical charge of 2.58×10^{-4} C in 1 kg of dry air. Damage to biological tissues, however, is proportional to the amount of energy absorbed by tissues, not air. The most common unit used to measure the effects of radiation on biological tissue is the **rad (radiation absorbed dose)**; the SI equivalent is the gray (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

$$1 \text{ rad} = 0.010 \text{ J/kg} \qquad 1 \text{ Gy} = 1 \text{ J/kg} \tag{19.4.2}$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs 0.010 J/70 kg = 1.4×10^{-4} J, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a 3.8×10^{-5} g droplet of boiling water. Because the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays. Thus a unit called the **rem (roentgen equivalent in man)** was devised to describe the actual amount of tissue damage caused by a given amount of radiation. The number of rems of radiation is equal to the number of rads multiplied by the RBE (relative biological effectiveness) factor, which is 1 for β particles, γ rays, and x-rays and about 20 for α particles. Because actual radiation doses tend to be very small, most measurements are reported in millirems (1 mrem = 10^{-3} rem).

Wilhelm Röntgen

Born in the Lower Rhine Province of Germany, Röntgen was the only child of a cloth manufacturer and merchant. His family moved to the Netherlands where he showed no particular aptitude in school, but where he was fond of roaming the countryside. Röntgen was expelled from technical school in Utrecht after being unjustly accused of drawing a caricature of one of the teachers. He began studying mechanical engineering in Zurich, which he could enter without having the credentials of a regular student, and received a PhD at the University of Zurich in 1869. In 1876 he became professor of physics.

Natural Sources of Radiation

We are continuously exposed to measurable background radiation from a variety of natural sources, which, on average, is equal to about 150–600 mrem/yr (Figure 19.4.3). One component of background radiation is *cosmic rays*, high-energy particles and γ rays emitted by the sun and other stars, which bombard Earth continuously. Because cosmic rays are partially absorbed by the atmosphere before they reach Earth's surface, the exposure of people living at sea level (about 30 mrem/yr) is significantly less than the exposure of people living at higher altitudes (about 50 mrem/yr in Denver, Colorado). Every 4 hours spent in an airplane at greater than 30,000 ft adds about 1 mrem to a person's annual radiation exposure.

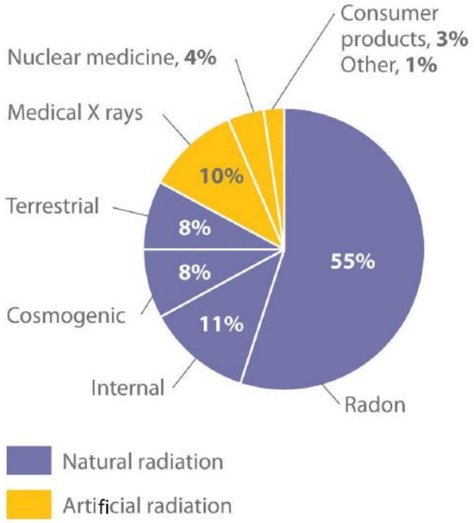


Figure 19.4.3: The Radiation Exposure of a Typical Adult in the United States. The average radiation dose from natural sources for an adult in the United States is about 150–600 mrem/yr. Radon accounts for more than half of an adult's total radiation exposure, whereas background radiation (terrestrial and cosmogenic) and exposure from medical sources account for about 15% each. Data source: Office of Civilian Radioactive Waste Management (CC BY-SA-NC; anonymous)

A second component of background radiation is *cosmogenic radiation*, produced by the interaction of cosmic rays with gases in the upper atmosphere. When high-energy cosmic rays collide with oxygen and nitrogen atoms, neutrons and protons are released. These, in turn, react with other atoms to produce radioactive isotopes, such as ^{14}C:

$$^{14}_{7}\mathrm{N} + ^{1}_{0}\mathrm{n} \rightarrow ^{14}_{6}\mathrm{C} + ^{1}_{1}\mathrm{p} \tag{19.4.3}$$

The carbon atoms react with oxygen atoms to form CO_2, which is eventually washed to Earth's surface in rain and taken up by plants. About 1 atom in 1×10^{12} of the carbon atoms in our bodies is radioactive ^{14}C, which decays by beta emission. About 5000

^{14}C nuclei disintegrate in your body during the 15 s or so that it takes you to read this paragraph. Tritium (^{3}H) is also produced in the upper atmosphere and falls to Earth in precipitation. The total radiation dose attributable to ^{14}C is estimated to be 1 mrem/yr, while that due to ^{3}H is about 1000 times less.

The third major component of background radiation is *terrestrial radiation*, which is due to the remnants of radioactive elements that were present on primordial Earth and their decay products. For example, many rocks and minerals in the soil contain small amounts of radioactive isotopes, such as $^{232}\mathrm{Th}$ and $^{238}\mathrm{U}$ as well as radioactive daughter isotopes, such as$^{226}\mathrm{Ra}$. The amount of background radiation from these sources is about the same as that from cosmic rays (approximately 30 mrem/yr). These isotopes are also found in small amounts in building materials derived from rocks and minerals, which significantly increases the radiation exposure for people who live in brick or concrete-block houses (60–160 mrem/yr) instead of houses made of wood (10–20 mrem/yr). Our tissues also absorb radiation (about 40 mrem/yr) from naturally occurring radioactive elements that are present in our bodies. For example, the average adult contains about 140 g of potassium as the K^+ ion. Naturally occurring potassium contains 0.0117% $^{40}\mathrm{K}$, which decays by emitting both a β particle and a (\gamma\) ray. In the last 20 seconds, about the time it took you to read this paragraph, approximately 40,000 $^{40}\mathrm{K}$ nuclei disintegrated in your body.

By far the most important source of background radiation is radon, the heaviest of the noble gases (group 18). Radon-222 is produced during the decay of^{238}U, and other isotopes of radon are produced by the decay of other heavy elements. Even though radon is chemically inert, all its isotopes are radioactive. For example, ^{222}Rn undergoes two successive alpha-decay events to give ^{214}Pb:

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{4}_{2}\alpha + {}^{218}_{84}\mathrm{Po} + {}^{4}_{2}\alpha + {}^{214}_{82}\mathrm{Pb} \tag{19.4.4}$$

Because radon is a dense gas, it tends to accumulate in enclosed spaces such as basements, especially in locations where the soil contains greater-than-average amounts of naturally occurring uranium minerals. Under most conditions, radioactive decay of radon poses no problems because of the very short range of the emitted α particle. If an atom of radon happens to be in your lungs when it decays, however, the chemically reactive daughter isotope polonium-218 can become irreversibly bound to molecules in the lung tissue. Subsequent decay of $^{218}\mathrm{Po}$ releases an α particle directly into one of the cells lining the lung, and the resulting damage can eventually cause lung cancer. The $^{218}\mathrm{Po}$ isotope is also readily absorbed by particles in cigarette smoke, which adhere to the surface of the lungs and can hold the radioactive isotope in place. Recent estimates suggest that radon exposure is a contributing factor in about 15% of the deaths due to lung cancer. Because of the potential health problem radon poses, many states require houses to be tested for radon before they can be sold. By current estimates, radon accounts for more than half of the radiation exposure of a typical adult in the United States.

Artificial Sources of Radiation

In addition to naturally occurring background radiation, humans are exposed to small amounts of radiation from a variety of artificial sources. The most important of these are the x-rays used for diagnostic purposes in medicine and dentistry, which are photons with much lower energy than γ rays. A single chest x-ray provides a radiation dose of about 10 mrem, and a dental x-ray about 2–3 mrem. Other minor sources include television screens and computer monitors with cathode-ray tubes, which also produce x-rays. Luminescent paints for watch dials originally used radium, a highly toxic alpha emitter if ingested by those painting the dials. Radium was replaced by tritium (^{3}H) and promethium (^{147}Pr), which emit low-energy β particles that are absorbed by the watch crystal or the glass covering the instrument. Radiation exposure from television screens, monitors, and luminescent dials totals about 2 mrem/yr. Residual fallout from previous atmospheric nuclear-weapons testing is estimated to account for about twice this amount, and the nuclear power industry accounts for less than 1 mrem/yr (about the same as a single 4 h jet flight).

✓ Example 19.4.1

Calculate the annual radiation dose in rads a typical 70 kg chemistry student receives from the naturally occurring ^{40}K in his or her body, which contains about 140 g of potassium (as the K^+ ion). The natural abundance of ^{40}K is 0.0117%. Each 1.00 mol of ^{40}K undergoes 1.05×10^7 decays/s, and each decay event is accompanied by the emission of a 1.32 MeV β particle.

Given: mass of student, mass of isotope, natural abundance, rate of decay, and energy of particle

Asked for: annual radiation dose in rads

Strategy:

A. Calculate the number of moles of ^{40}K present using its mass, molar mass, and natural abundance.
B. Determine the number of decays per year for this amount of ^{40}K.
C. Multiply the number of decays per year by the energy associated with each decay event. To obtain the annual radiation dose, use the mass of the student to convert this value to rads.

Solution

A The number of moles of ^{40}K present in the body is the total number of potassium atoms times the natural abundance of potassium atoms present as ^{40}K divided by the atomic mass of ^{40}K:

$$\text{moles }{}^{40}\text{K} = 140 \text{ g K} \times \frac{0.0117 \text{ mol }{}^{40}\text{K}}{100 \text{ mol K}} \times \frac{1 \text{ mol K}}{40.0 \text{ g K}} = 4.10 \times 10^{-4} \text{ mol }{}^{40}\text{K}$$

B We are given the number of atoms of ^{40}K that decay per second in 1.00 mol of ^{40}K, so the number of decays per year is as follows:

$$\frac{\text{decays}}{\text{year}} = 4.10 \times 10^{-4} \text{ mol}^{40}\text{ K} \times \frac{1.05 \times 10^{7} \text{ decays/s}}{1.00 \text{ mol }{}^{40}\text{K}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{24 \text{ h}}{1 \text{ day}} \times \frac{365 \text{ days}}{1 \text{ yr}}$$

C The total energy the body receives per year from the decay of ^{40}K is equal to the total number of decays per year multiplied by the energy associated with each decay event:

$$\begin{aligned}\text{total energy per year} &= \frac{1.36 \times 10^{11} \text{ decays}}{\text{yr}} \times \frac{1.32 \text{ MeV}}{\text{decays}} \times \frac{10^{6} \text{ eV}}{\text{MeV}} \times \frac{1.602 \times 10^{-19} \text{ J}}{\text{eV}} \\ &= 2.87 \times 10^{-2} \text{ J/yr}\end{aligned}$$

We use the definition of the rad (1 rad = 10^{-2} J/kg of tissue) to convert this figure to a radiation dose in rads. If we assume the dose is equally distributed throughout the body, then the radiation dose per year is as follows:

$$\begin{aligned}\text{radiation dose per year} &= \frac{2.87 \times 10^{-2} \text{ J/yr}}{70.0 \text{ kg}} \times \frac{1 \text{ rad}}{1 \times 10^{-2} \text{ J/kg}} \\ &= 4.10 \times 10^{-2} \text{ rad/yr} = 41 \text{ mrad/yr}\end{aligned}$$

This corresponds to almost half of the normal background radiation most people experience.

Exercise 19.4.1

Because strontium is chemically similar to calcium, small amounts of the Sr^{2+} ion are taken up by the body and deposited in calcium-rich tissues such as bone, using the same mechanism that is responsible for the absorption of Ca^{2+}. Consequently, the radioactive strontium (^{90}Sr) found in fission waste and released by atmospheric nuclear-weapons testing is a major health concern. A normal 70 kg human body has about 280 mg of strontium, and each mole of ^{90}Sr undergoes 4.55×10^{14} decays/s by the emission of a 0.546 MeV β particle. What would be the annual radiation dose in rads for a 70 kg person if 0.10% of the strontium ingested were ^{90}Sr?

Answer

5.7×10^{3} rad/yr (which is 10 times the fatal dose)

Assessing the Impact of Radiation Exposure

One of the more controversial public policy issues debated today is whether the radiation exposure from artificial sources, when combined with exposure from natural sources, poses a significant risk to human health. The effects of single radiation doses of different magnitudes on humans are listed in Table 19.4.2 Because of the many factors involved in radiation exposure (length of exposure, intensity of the source, and energy and type of particle), it is difficult to quantify the specific dangers of one radioisotope versus another. Nonetheless, some general conclusions regarding the effects of radiation exposure are generally accepted as valid.

Table 19.4.2: The Effects of a Single Radiation Dose on a 70 kg Human

Dose (rem)	Symptoms/Effects
< 5	no observable effect
5–20	possible chromosomal damage
20–100	temporary reduction in white blood cell count
50–100	temporary sterility in men (up to a year)
100–200	mild radiation sickness, vomiting, diarrhea, fatigue; immune system suppressed; bone growth in children retarded
> 300	permanent sterility in women
> 500	fatal to 50% within 30 days; destruction of bone marrow and intestine
> 3000	fatal within hours

Radiation doses of 600 rem and higher are invariably fatal, while a dose of 500 rem kills half the exposed subjects within 30 days. Smaller doses (≤ 50 rem) appear to cause only limited health effects, even though they correspond to tens of years of natural radiation. This does not, however, mean that such doses have no ill effects; they may cause long-term health problems, such as cancer or genetic changes that affect offspring. The possible detrimental effects of the much smaller doses attributable to artificial sources (< 100 mrem/yr) are more difficult to assess.

The tissues most affected by large, whole-body exposures are bone marrow, intestinal tissue, hair follicles, and reproductive organs, all of which contain rapidly dividing cells. The susceptibility of rapidly dividing cells to radiation exposure explains why cancers are often treated by radiation. Because cancer cells divide faster than normal cells, they are destroyed preferentially by radiation. Long-term radiation-exposure studies on fruit flies show a linear relationship between the number of genetic defects and both the magnitude of the dose and the exposure time. In contrast, similar studies on mice show a much lower number of defects when a given dose of radiation is spread out over a long period of time rather than received all at once. Both patterns are plotted in Figure $19.4.4$, but which of the two is applicable to humans? According to one hypothesis, mice have very low risk from low doses because their bodies have ways of dealing with the damage caused by natural radiation. At much higher doses, however, their natural repair mechanisms are overwhelmed, leading to irreversible damage. Because mice are biochemically much more similar to humans than are fruit flies, many scientists believe that this model also applies to humans. In contrast, the linear model assumes that all exposure to radiation is intrinsically damaging and suggests that stringent regulation of low-level radiation exposure is necessary. Which view is more accurate? The answer—while yet unknown—has extremely important consequences for regulating radiation exposure.

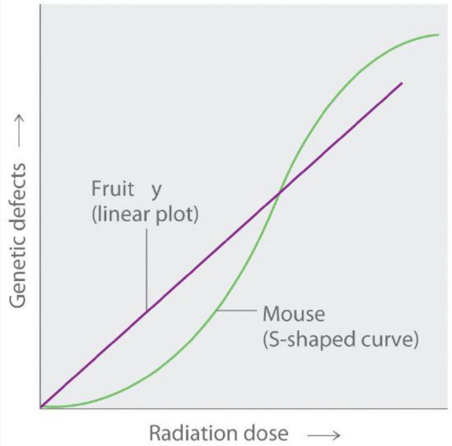


Figure 19.4.4: Two Possible Relationships between the Number of Genetic Defects and Radiation Exposure. Studies on fruit flies show a linear relationship between the number of genetic defects and the magnitude of the radiation dose and exposure time, which is consistent with a cumulative effect of radiation. In contrast, studies on mice show an S-shaped curve, which suggests that the number of defects is lower when radiation exposure occurs over a longer time. Which of these relationships is more applicable to humans is a matter of considerable debate. (CC BY-SA-NC; anonymous)

Graph of genetic defects against radiation dose. Fruit is graphed in purple and has a linear plot. Mouse is graphed in green and has a S shaped curve.

Summary

Nonionizing radiation is relatively low in energy and can be used as a heat source, whereas ionizing radiation, which is higher in energy, can penetrate biological tissues and is highly reactive. The effects of radiation on matter depend on the energy of the radiation. Nonionizing radiation is relatively low in energy, and the energy is transferred to matter in the form of heat. Ionizing radiation is relatively high in energy, and when it collides with an atom, it can completely remove an electron to form a positively charged ion that can damage biological tissues. Alpha particles do not penetrate very far into matter, whereas γ rays penetrate more deeply. Common units of radiation exposure, or dose, are the roentgen (R), the amount of energy absorbed by dry air, and the rad (radiation absorbed dose), the amount of radiation that produces 0.01 J of energy in 1 kg of matter. The rem (roentgen equivalent in man) measures the actual amount of tissue damage caused by a given amount of radiation. Natural sources of radiation include cosmic radiation, consisting of high-energy particles and γ rays emitted by the sun and other stars; cosmogenic radiation, which is produced by the interaction of cosmic rays with gases in the upper atmosphere; and terrestrial radiation, from radioactive elements present on primordial Earth and their decay products. The risks of ionizing radiation depend on the intensity of the radiation, the mode of exposure, and the duration of the exposure.

19.5: Nuclear Fission

Only very massive nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that have different atomic numbers and atomic masses. This process is most important for the transactinide elements, with $Z \geq 104$. Spontaneous fission is invariably accompanied by the release of large amounts of energy, and it is usually accompanied by the emission of several neutrons as well. An example is the spontaneous fission of $^{254}_{98}\text{Cf}$, which gives a distribution of fission products; one possible set of products is shown in the following equation:

$$^{254}_{98}\text{Cf} \rightarrow {}^{118}_{46}\text{Pd} + {}^{132}_{52}\text{Te} + 4^1_0\text{n} \tag{19.5.1}$$

Once again, the number of nucleons is conserved. Thus the sum of the mass numbers of the products (118 + 132 + 4 = 254) equals the mass number of the reactant. Similarly, the sum of the atomic numbers of the products [46 + 52 + (4 × 0) = 98] is the same as the atomic number of the parent nuclide.

✓ Example 19.5.1

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of $^{35}_{16}\text{S}$
b. the decay of $^{201}_{80}\text{Hg}$ by electron capture
c. the decay of $^{30}_{15}\text{P}$ by positron emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

A Identify the reactants and the products from the information given.

B Use the values of A and Z to identify any missing components needed to balance the equation.

Solution

a.

A We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product as ^A_ZX:

$$^{35}_{16}\text{S} \rightarrow {}^A_Z\text{X} + {}^0_{-1}\beta \tag{19.5.2}$$

B Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of $A = 35 - 0 = 35$ and an atomic number of $Z = 16 - (-1) = 17$. The element with $Z = 17$ is chlorine, so the balanced nuclear equation is as follows:

$$^{35}_{16}\text{S} \rightarrow {}^{35}_{17}\text{Cl} + {}^0_{-1}\beta \tag{19.5.3}$$

b.

A We know the identities of both reactants: $^{201}_{80}\text{Hg}$ and an inner electron, $^0_{-1}\text{e}$. The reaction is as follows:

$$^{201}_{80}\text{Hg} + {}^0_{-1}\text{e} \rightarrow {}^A_Z\text{X}$$

B Both protons and neutrons are conserved, so the mass number of the product must be $A = 201 + 0 = 201$, and the atomic number of the product must be $Z = 80 + (-1) = 79$, which corresponds to the element gold. The balanced nuclear equation is thus

$$^{201}_{80}\text{Hg} + {}^0_{-1}\text{e} \rightarrow {}^{201}_{79}\text{Au}$$

c.

A As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore

$$^{30}_{15}\text{P} \rightarrow {}^A_Z\text{X} + {}^0_{+1}\beta$$

B The mass number of the second product is $A = 30 - 0 = 30$, and its atomic number is $Z = 15 - 1 = 14$, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:

$${}^{30}_{15}\text{P} \rightarrow {}^{30}_{14}\text{Si} + {}^{0}_{+1}\beta$$

? Exercise 19.5.1

Write a balanced nuclear equation to describe each reaction.

a. ${}^{11}_{6}\text{C}$ by positron emission
b. the beta decay of molybdenum-99
c. the emission of an α particle followed by gamma emission from ${}^{185}_{74}\text{W}$

Answer

a. ${}^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}\beta$
b. ${}^{99}_{42}\text{Mo} \rightarrow {}^{99m}_{43}\text{Tc} + {}^{0}_{-1}\beta$
c. ${}^{185}_{74}\text{W} \rightarrow {}^{181}_{72}\text{Hf} + {}^{4}_{2}\alpha + {}^{0}_{0}\gamma$

✓ Example 19.5.2

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. ${}^{45}_{22}\text{Ti}$
b. ${}^{242}_{94}\text{Pu}$
c. ${}^{12}_{5}\text{B}$
d. ${}^{256}_{100}\text{Fm}$

Given: nuclide

Asked for: type of nuclear decay

Strategy:

Based on the neutron-to-proton ratio and the value of Z, predict the type of nuclear decay reaction that will produce a more stable nuclide.

Solution

a. This nuclide has a neutron-to-proton ratio of only 1.05, which is much less than the requirement for stability for an element with an atomic number in this range. Nuclei that have low neutron-to-proton ratios decay by converting a proton to a neutron. The two possibilities are positron emission, which converts a proton to a neutron and a positron, and electron capture, which converts a proton and a core electron to a neutron. In this case, both are observed, with positron emission occurring about 86% of the time and electron capture about 14% of the time.
b. Nuclei with $Z > 83$ are too heavy to be stable and usually undergo alpha decay, which decreases both the mass number and the atomic number. Thus ${}^{242}_{94}\text{Pu}$ is expected to decay by alpha emission.
c. This nuclide has a neutron-to-proton ratio of 1.4, which is very high for a light element. Nuclei with high neutron-to-proton ratios decay by converting a neutron to a proton and an electron. The electron is emitted as a β particle, and the proton remains in the nucleus, causing an increase in the atomic number with no change in the mass number. We therefore predict that ${}^{12}_{5}\text{B}$ will undergo beta decay.
d. This is a massive nuclide, with an atomic number of 100 and a mass number much greater than 200. Nuclides with $A \geq 200$ tend to decay by alpha emission, and even heavier nuclei tend to undergo spontaneous fission. We therefore predict that ${}^{256}_{100}\text{Fm}$ will decay by either or both of these two processes. In fact, it decays by both spontaneous fission and alpha emission, in a 97:3 ratio.

? Exercise 19.5.2

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. ${}^{32}_{14}\text{Si}$

b. ${}^{43}_{21}\text{Sc}$
c. ${}^{231}_{91}\text{Pa}$

Answer

a. beta decay
b. positron emission or electron capture
c. alpha decay

19.6: Nuclear Fusion and Nucleosynthesis

Learning Objectives

- Describe the nuclear reactions in a nuclear fusion reaction
- Quantify the energy released or absorbed in a fusion reaction

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called fusion. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:

$$4\,{}^{1}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + 2\,{}^{0}_{+1}\text{n} \tag{19.6.1}$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about 3.6 × 10^{11} kJ of energy per mole of ${}^{4}_{2}\text{He}$ produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 (1.8 × 10^{10} kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

It has been determined that the nuclei of the heavy isotopes of hydrogen, a deuteron, ${}^{2}_{1}H$ and a triton, ${}^{3}_{1}H$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$${}^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + 2\,{}^{1}_{0}\text{n} \tag{19.6.2}$$

This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69 × 10^{9} kilojoules per mole of ${}^{4}_{2}\text{He}$ formed. The very high temperature is necessary to give the nuclei enough kinetic energy to overcome the very strong repulsive forces resulting from the positive charges on their nuclei so they can collide.

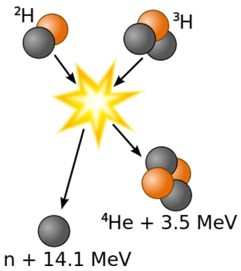


Figure 19.6.1: Fusion of deuterium with tritium creating helium-4, freeing a neutron, and releasing 17.59 MeV of energy, as an appropriate amount of mass changing forms to appear as the kinetic energy of the products, in agreement with kinetic $E = \Delta mc^2$, where Δm is the change in rest mass of particles.[Image use with permission via Wikipedia (Wykis)

The most important fusion process in nature is the one that powers stars. In the 20th century, it was realized that the energy released from nuclear fusion reactions accounted for the longevity of the Sun and other stars as a source of heat and light. The fusion of nuclei in a star, starting from its initial hydrogen and helium abundance, provides that energy and synthesizes new nuclei as a byproduct of that fusion process. The prime energy producer in the Sun is the fusion of hydrogen to form helium, which occurs at a solar-core temperature of 14 million kelvin. The net result is the fusion of four protons into one alpha particle, with the release of two positrons, two neutrinos (which changes two of the protons into neutrons), and energy (Figure $19.6.2$).

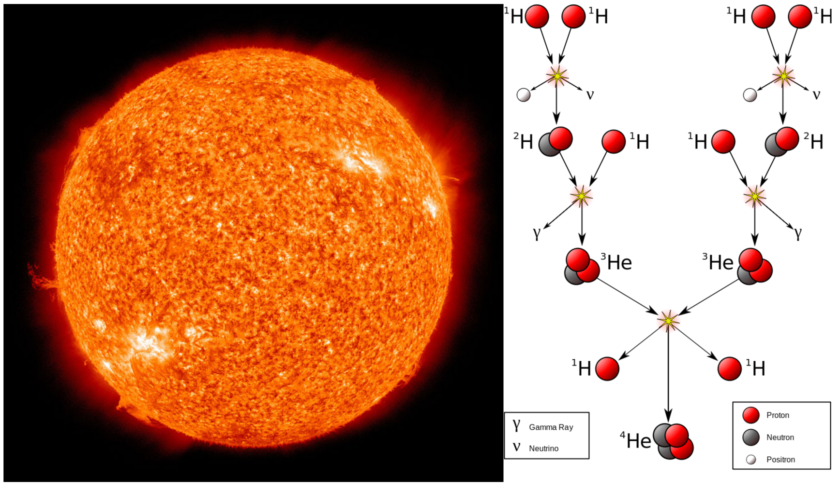


Figure 19.6.2: (left) The Sun is a main-sequence star, and thus generates its energy by nuclear fusion of hydrogen nuclei into helium. In its core, the Sun fuses 620 million metric tons of hydrogen each second. (right) The proton-proton chain dominates in stars the size of the Sun or smaller.

Example 19.6.1

Calculate the energy released in each of the following hypothetical processes.

a. $3\,{}^{4}_{2}\mathrm{He} \rightarrow {}^{12}_{6}\mathrm{C}$
b. $6\,{}^{1}_{1}\mathrm{H} + 6\,{}^{1}_{0}\mathrm{n} \rightarrow {}^{12}_{6}\mathrm{C}$
c. $6\,{}^{2}_{1}\mathrm{D} \rightarrow {}^{12}_{6}\mathrm{C}$

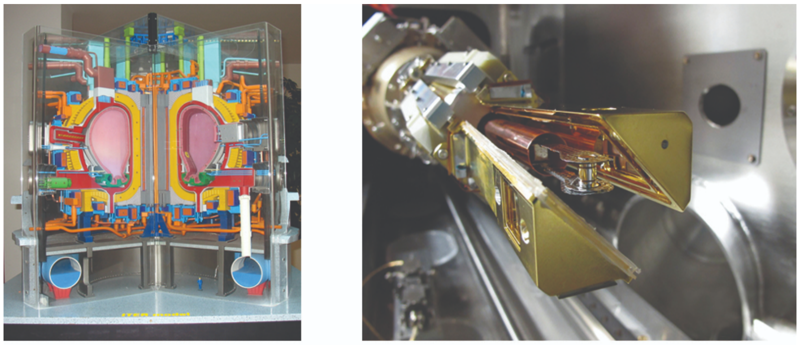
Solution

a. $Q_a = 3 \times 4.0026 - 12.000)\,amu \times (1.4924 \times 10^{-10}\ J/amu) = 1.17 \times 10^{-12}\ J$
b. $Q_b = (6 \times (1.007825 + 1.008665) - 12.00000)\,amu \times (1.4924 \times 10^{1-0} J/amu) = 1.476 \times 10^{-11}\ J$
c. $Q_c = 6 \times 2.014102 - 12.00000\,amu \times (1.4924 \times 10^{-10}\ J/amu) = 1.263 \times 10^{-11}\ J$

Fusion of He to give C releases the least amount of energy, because the fusion to produce He has released a large amount. The difference between the second and the third is the binding energy of deuterium. The conservation of mass-and-energy is well illustrated in these calculations. On the other hand, the calculation is based on the conservation of mass-and-energy.

Nuclear Reactors

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.



(a) (b)

Figure 19.6.3: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving larg\times 10^{scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

Another much more beneficial way to create fusion reactions is in a fusion reactor, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure 19.6.3). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. At the time of this writing, there are no self-sustaining fusion reactors operating in the world, although small-scale controlled fusion reactions have been run for very brief periods.Contributors

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

CHAPTER OVERVIEW

20: Molecular Spectroscopy and Photochemistry

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI
XVII XVIII XIX XX XXI XXII XXIII • **Homework Exercises**

Template:HideTOC

Spectroscopy is the use of the absorption, emission, or scattering of electromagnetic radiation by atoms or molecules (or atomic or molecular ions) to qualitatively or quantitatively study the atoms or molecules, or to study physical processes. The interaction of radiation with matter can cause redirection of the radiation and/or transitions between the energy levels of the atoms or molecules. A transition from a lower level to a higher level with transfer of energy from the radiation field to the atom or molecule is called absorption. A transition from a higher level to a lower level is called emission if energy is transferred to the radiation field, or nonradiative decay if no radiation is emitted. Redirection of light due to its interaction with matter is called scattering, and may or may not occur with transfer of energy, i.e., the scattered radiation has a slightly different or the same wavelength.

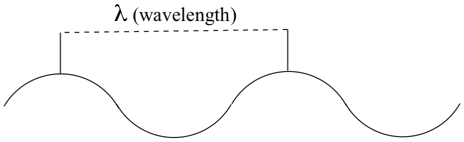
Topic hierarchy

20.1: General Aspects of Molecular Spectroscopy

The electromagnetic spectrum

Electromagnetic radiation, as you may recall from a previous chemistry or physics class, is composed of electrical and magnetic waves which oscillate on perpendicular planes. Visible light is electromagnetic radiation. So are the gamma rays that are emitted by spent nuclear fuel, the x-rays that a doctor uses to visualize your bones, the ultraviolet light that causes a painful sunburn when you forget to apply sun block, the infrared light that the army uses in night-vision goggles, the microwaves that you use to heat up your frozen burritos, and the radio-frequency waves that bring music to anybody who is old-fashioned enough to still listen to FM or AM radio.

Just like ocean waves, electromagnetic waves travel in a defined direction. While the speed of ocean waves can vary, however, the speed of electromagnetic waves – commonly referred to as the speed of light – is essentially a constant, approximately 300 million meters per second. This is true whether we are talking about gamma radiation or visible light. Obviously, there is a big difference between these two types of waves – we are surrounded by the latter for more than half of our time on earth, whereas we hopefully never become exposed to the former to any significant degree. The different properties of the various types of electromagnetic radiation are due to differences in their wavelengths, and the corresponding differences in their energies: *shorter wavelengths correspond to higher energy.*



High-energy radiation (such as gamma- and x-rays) is composed of very short waves – as short as 10^{-16} meter from crest to crest. Longer waves are far less energetic, and thus are less dangerous to living things. Visible light waves are in the range of 400 – 700 nm (nanometers, or 10^{-9} m), while radio waves can be several hundred meters in length.

The notion that electromagnetic radiation contains a quantifiable amount of energy can perhaps be better understood if we talk about light as a stream of *particles*, called **photons**, rather than as a wave. (Recall the concept known as 'wave-particle duality': at the quantum level, wave behavior and particle behavior become indistinguishable, and very small particles have an observable 'wavelength'). If we describe light as a stream of photons, the energy of a particular wavelength can be expressed as:

$$E = \frac{hc}{\lambda} \tag{4.1.1}$$

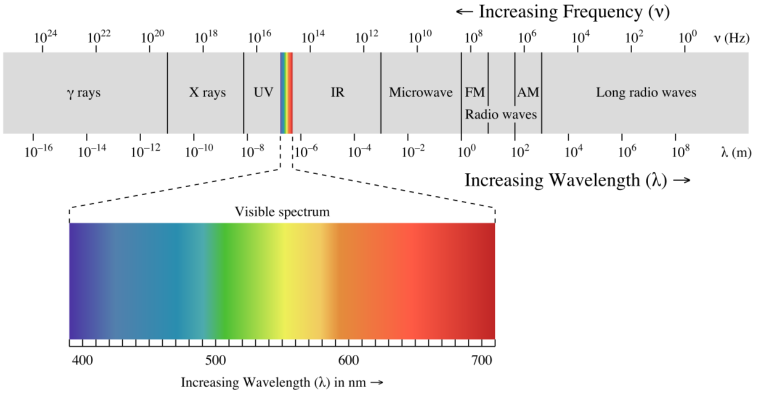
where E is energy in kJ/mol, **λ** (the Greek letter *lambda*) is wavelength in meters, *c* is 3.00 x 10^8 m/s (the speed of light), and *h* is 3.99 x 10^{-13} kJ·s·mol^{-1}, a number known as **Planck's constant**.

Because electromagnetic radiation travels at a constant speed, each wavelength corresponds to a given frequency, which is the number of times per second that a crest passes a given point. Longer waves have lower frequencies, and shorter waves have higher frequencies. Frequency is commonly reported in hertz (Hz), meaning 'cycles per second', or 'waves per second'. The standard unit for frequency is s^{-1}.

When talking about electromagnetic waves, we can refer either to wavelength or to frequency - the two values are interconverted using the simple expression:

$$\lambda\nu = c \tag{4.1.2}$$

where **ν** (the Greek letter '*nu*') is frequency in s^{-1}. Visible red light with a wavelength of 700 nm, for example, has a frequency of 4.29 x 10^{14} Hz, and an energy of 40.9 kcal per mole of photons. The full range of electromagnetic radiation wavelengths is referred to as the **electromagnetic spectrum**.



(Image from Wikipedia commons)

Notice that visible light takes up just a narrow band of the full spectrum. White light from the sun or a light bulb is a mixture of all of the visible wavelengths. You see the visible region of the electromagnetic spectrum divided into its different wavelengths every time you see a rainbow: violet light has the shortest wavelength, and red light has the longest.

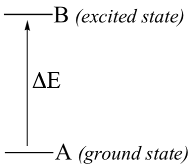
Exercise 4.4: Visible light has a wavelength range of about 400-700 nm. What is the corresponding frequency range? What is the corresponding energy range, in kJ/mol of photons?

Solutions

Overview of a molecular spectroscopy experiment

In a spectroscopy experiment, electromagnetic radiation of a specified range of wavelengths is allowed to pass through a sample containing a compound of interest. The sample molecules absorb energy from some of the wavelengths, and as a result jump from a low energy ‘ground state’ to some higher energy ‘excited state’. Other wavelengths are *not* absorbed by the sample molecule, so they pass on through. A detector on the other side of the sample records which wavelengths were absorbed, and to what extent they were absorbed.

Here is the key to molecular spectroscopy: *a given molecule will specifically absorb only those wavelengths which have energies that correspond to the energy difference of the transition that is occurring*. Thus, if the transition involves the molecule jumping from ground state A to excited state B, with an energy difference of **Δ**E, the molecule will specifically absorb radiation with wavelength that corresponds to **Δ**E, while allowing other wavelengths to pass through unabsorbed.



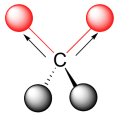
By observing which wavelengths a molecule absorbs, and to what extent it absorbs them, we can gain information about the nature of the energetic transitions that a molecule is able to undergo, and thus information about its structure.

These generalized ideas may all sound quite confusing at this point, but things will become much clearer as we begin to discuss specific examples.

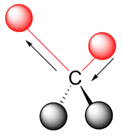
Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

20.2: Vibrations and Rotations of Molecules: Infrared and Microwave Spectroscopy

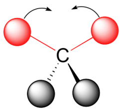
Covalent bonds in organic molecules are not rigid sticks – rather, they behave more like springs. At room temperature, organic molecules are always in motion, as their bonds stretch, bend, and twist. These complex vibrations can be broken down mathematically into individual **vibrational modes**, a few of which are illustrated below.



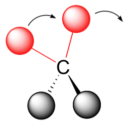
symmetric stretching



asymmetric stretching



scissoring

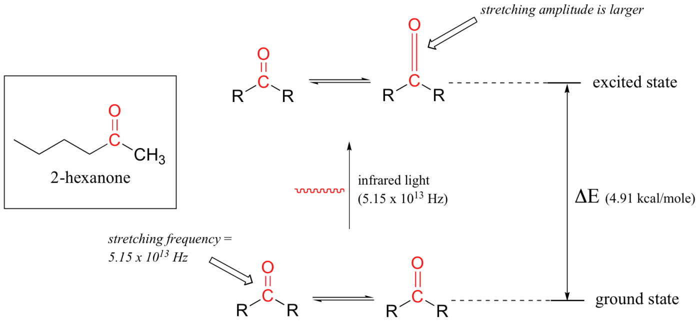


rocking

The energy of molecular vibration is *quantized* rather than continuous, meaning that a molecule can only stretch and bend at certain 'allowed' frequencies. If a molecule is exposed to electromagnetic radiation that matches the frequency of one of its vibrational modes, it will in most cases absorb energy from the radiation and jump to a higher vibrational energy state - what this means is that the *amplitude* of the vibration will increase, but the vibrational *frequency* will remain the same. The difference in energy between the two vibrational states is equal to the energy associated with the wavelength of radiation that was absorbed. It turns out that it is the *infrared* region of the electromagnetic spectrum which contains frequencies corresponding to the vibrational frequencies of organic bonds.

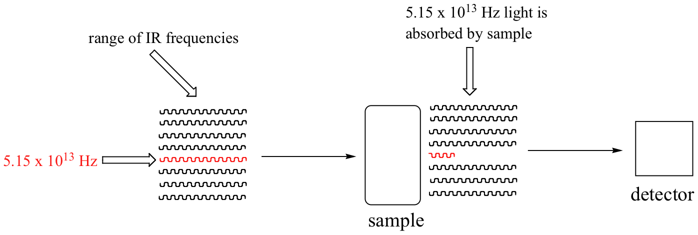
Let's take 2-hexanone as an example. Picture the carbonyl bond of the ketone group as a spring that is constantly bouncing back and forth, stretching and compressing, pushing the carbon and oxygen atoms further apart and then pulling them together. This is the **stretching mode** of the carbonyl bond. In the space of one second, the spring 'bounces' back and forth 5.15 x 10^{13} times - in other words, the ground-state frequency of carbonyl stretching for a the ketone group is about 5.15 x 10^{13} Hz.

If our ketone sample is irradiated with infrared light, the carbonyl bond will specifically absorb light with this same frequency, which by equations 4.1 and 4.2 corresponds to a wavelength of 5.83 x 10^{-6} m and an energy of 4.91 kcal/mol. When the carbonyl bond absorbs this energy, it jumps up to an excited vibrational state.



The value of **Δ**E - the energy difference between the low energy (ground) and high energy (excited) vibrational states - is equal to 4.91 kcal/mol, the same as the energy associated with the absorbed light frequency. The molecule does not remain in its excited vibrational state for very long, but quickly releases energy to the surrounding environment in form of heat, and returns to the ground state.

With an instrument called an infrared spectrophotometer, we can 'see' this vibrational transition. In the spectrophotometer, infrared light with frequencies ranging from about 10^{13} to 10^{14} Hz is passed though our sample of cyclohexane. Most frequencies pass right through the sample and are recorded by a detector on the other side.



Our 5.15 x 10^{13} Hz carbonyl stretching frequency, however, is absorbed by the 2-hexanone sample, and so the detector records that the intensity of this frequency, after having passed through the sample, is something less than 100% of its initial intensity.

The vibrations of a 2-hexanone molecule are not, of course, limited to the simple stretching of the carbonyl bond. The various carbon-carbon bonds also stretch and bend, as do the carbon-hydrogen bonds, and all of these vibrational modes also absorb different frequencies of infrared light.

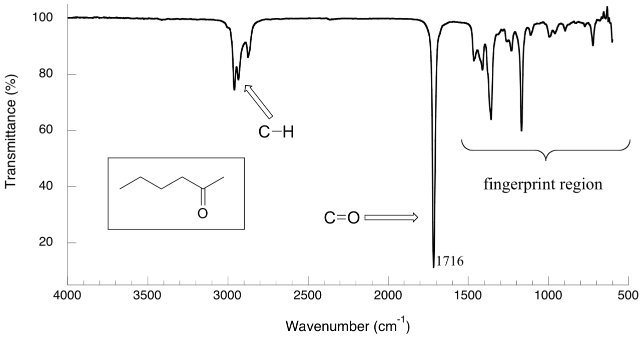
The power of infrared spectroscopy arises from the observation that *different functional groups have different characteristic absorption frequencies*. The carbonyl bond in a ketone, as we saw with our 2-hexanone example, typically absorbs in the range of 5.11 - 5.18 x 10^{13} Hz, depending on the molecule. The carbon-carbon triple bond of an alkyne, on the other hand, absorbs in the range 6.30 - 6.80 x 10^{13} Hz. The technique is therefore very useful as a means of identifying which functional groups are present in a molecule of interest. If we pass infrared light through an unknown sample and find that it absorbs in the carbonyl frequency range but not in the alkyne range, we can infer that the molecule contains a carbonyl group but not an alkyne.

Some bonds absorb infrared light more strongly than others, and some bonds do not absorb at all. *In order for a vibrational mode to absorb infrared light, it must result in a periodic change in the dipole moment of the molecule*. Such vibrations are said to be **infrared active**. In general, the greater the polarity of the bond, the stronger its IR absorption. The carbonyl bond is very polar, and absorbs very strongly. The carbon-carbon triple bond in most alkynes, in contrast, is much less polar, and thus a stretching vibration does not result in a large change in the overall dipole moment of the molecule. Alkyne groups absorb rather weakly compared to carbonyls.

Some kinds of vibrations are **infrared inactive**. The stretching vibrations of completely symmetrical double and triple bonds, for example, do not result in a change in dipole moment, and therefore do not result in any absorption of light (but other bonds and vibrational modes in these molecules *do* absorb IR light).

infrared-inactive double and triple bonds

Now, let's look at some actual output from IR spectroscopy experiments. Below is the IR spectrum for 2-hexanone.



There are a number of things that need to be explained in order for you to understand what it is that we are looking at. On the horizontal axis we see IR wavelengths expressed in terms of a unit called **wavenumber** (cm^{-1}), which tells us how many waves fit into one centimeter. On the vertical axis we see '**% transmittance**', which tells us how strongly light was absorbed at each frequency (100% transmittance means no absorption occurred at that frequency). The solid line traces the values of %

transmittance for every wavelength – the ‘peaks’ (which are actually pointing down) show regions of strong absorption. For some reason, it is typical in IR spectroscopy to report wavenumber values rather than wavelength (in meters) or frequency (in Hz). The ‘upside down’ vertical axis, with absorbance peaks pointing down rather than up, is also a curious convention in IR spectroscopy. We wouldn’t want to make things too easy for you!

Exercise 4.5: : Express the wavenumber value of 3000 cm^{-1} in terms of wavelength (in meter units) frequency (in Hz), and associated energy (in kJ/mol).

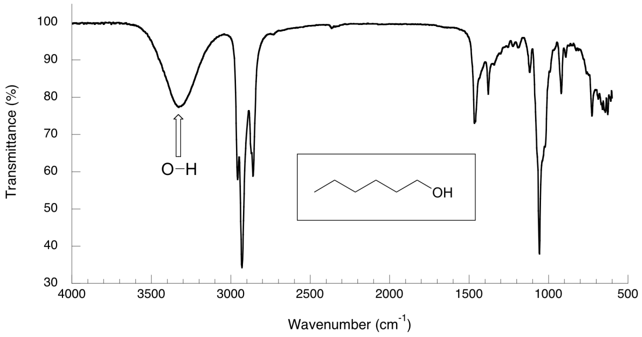
Solutions

The key absorption peak in this spectrum is that from the carbonyl double bond, at 1716 cm^{-1} (corresponding to a wavelength of 5.86 mm, a frequency of 5.15 x 10^{13} Hz, and a **Δ**E value of 4.91 kcal/mol). Notice how strong this peak is, relative to the others on the spectrum: *a strong peak in the 1650-1750 cm^{-1} region is a dead giveaway for the presence of a carbonyl group*. Within that range, carboxylic acids, esters, ketones, and aldehydes tend to absorb in the shorter wavelength end (1700-1750 cm-1), while conjugated unsaturated ketones and amides tend to absorb on the longer wavelength end (1650-1700 cm^{-1}).

The jagged peak at approximately 2900-3000 cm^{-1} is characteristic of tetrahedral carbon-hydrogen bonds. This peak is not terribly useful, as just about every organic molecule that you will have occasion to analyze has these bonds. Nevertheless, it can serve as a familiar reference point to orient yourself in a spectrum.

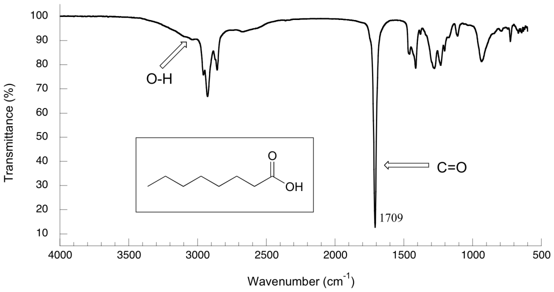
You will notice that there are many additional peaks in this spectrum in the longer-wavelength 400 -1400 cm^{-1} region. This part of the spectrum is called the **fingerprint region**. While it is usually very difficult to pick out any specific functional group identifications from this region, it does, nevertheless, contain valuable information. The reason for this is suggested by the name: just like a human fingerprint, the pattern of absorbance peaks in the fingerprint region is unique to every molecule, meaning that the data from an unknown sample can be compared to the IR spectra of known standards in order to make a positive identification. It was the IR fingerprint region of the suspicious yellow paint that allowed for its identification as a pigment that could not possibly have been used by the purported artist, William Aiken Walker.

Now, let’s take a look at the IR spectrum for 1-hexanol.



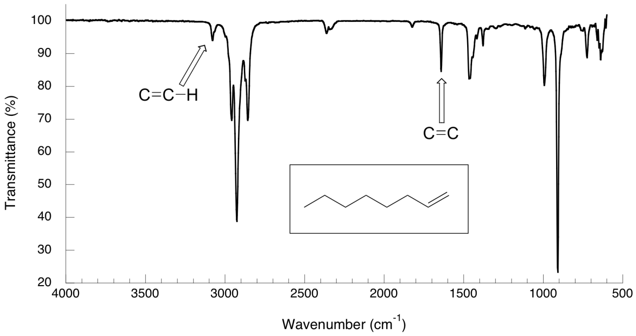
As you can see, the carbonyl peak is gone, and in its place is a very broad ‘mountain’ centered at about 3400 cm^{-1}. This signal is characteristic of the O-H stretching mode of alcohols, and is a dead giveaway for the presence of an alcohol group. The breadth of this signal is a consequence of hydrogen bonding between molecules.

In the spectrum of octanoic acid we see, as expected, the characteristic carbonyl peak, this time at 1709 cm^{-1}.



We also see a low, broad absorbance band that looks like an alcohol, except that it is displaced slightly to the right (long-wavelength) side of the spectrum, causing it to overlap to some degree with the C-H region. This is the characteristic carboxylic acid O-H single bond stretching absorbance.

The spectrum for 1-octene shows two peaks that are characteristic of alkenes: the one at 1642 cm^{-1} is due to stretching of the carbon-carbon double bond, and the one at 3079 cm-1 is due to stretching of the s bond between the alkene carbons and their attached hydrogens.



Alkynes have characteristic IR absorbance peaks in the range of 2100-2250 cm^{-1} due to stretching of the carbon-carbon triple bond, and terminal alkenes can be identified by their absorbance at about 3300 cm-1, due to stretching of the bond between the sp-hybridized carbon and the terminal hydrogen.

You can see many more examples of IR spectra in the Spectral Database for Organic Compounds

Exercise 4.6: Explain how you could use the C-C and C-H stretching frequencies in IR spectra to distinguish between four constitutional isomers: 1,2-dimethylcyclohexene, 1,3-octadiene, 3-octyne, and 1-octyne.

Exercise 4.7: Using the online Spectral Database for Organic Compounds, look up IR spectra for the following compounds, and identify absorbance bands corresponding to those listed in the table above. List actual frequencies for each signal to the nearest cm^{-1} unit, using the information in tables provided on the site.

a) 1-methylcyclohexanol

b) 4-methylcyclohexene

c) 1-hexyne

d) 2-hexyne

e) 3-hexyne-2,5-diol

Exercise 4.8: A carbon-carbon single bond absorbs in the fingerprint region, and we have already seen the characteristic absorption wavelengths of carbon-carbon double and triple bonds. Rationalize the trend in wavelengths. (*Hint* - remember, we are thinking of bonds as springs, and looking at the frequency at which they 'bounce').

Solutions

It is possible to identify other functional groups such as amines and ethers, but the characteristic peaks for these groups are considerably more subtle and/or variable, and often are overlapped with peaks from the fingerprint region. For this reason, we will limit our discussion here to the most easily recognized functional groups, which are summarized in table 1 in the tables section at the end of the text.

As you can imagine, obtaining an IR spectrum for a compound will not allow us to figure out the complete structure of even a simple molecule, unless we happen to have a reference spectrum for comparison. In conjunction with other analytical methods, however, IR spectroscopy can prove to be a very valuable tool, given the information it provides about the presence or absence of key functional groups. IR can also be a quick and convenient way for a chemist to check to see if a reaction has proceeded as planned. If we were to run a reaction in which we wished to convert cyclohexanone to cyclohexanol, for example, a quick comparison of the IR spectra of starting compound and product would tell us if we had successfully converted the ketone group to an alcohol (this type of reaction is discussed in detail in chapter 16).

Kahn Academy video tutorials on infrared spectroscopy

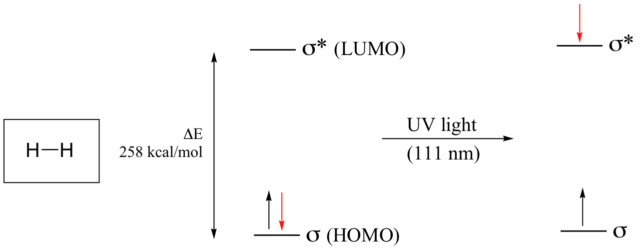
Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

20.3: Excited Electronic States: Electronic Spectroscopy of Molecules

While interaction with infrared light causes molecules to undergo vibrational transitions, the shorter wavelength, higher energy radiation in the UV (200-400 nm) and visible (400-700 nm) range of the electromagnetic spectrum causes many organic molecules to undergo **electronic transitions**. What this means is that when the energy from UV or visible light is absorbed by a molecule, one of its electrons jumps from a lower energy to a higher energy molecular orbital.

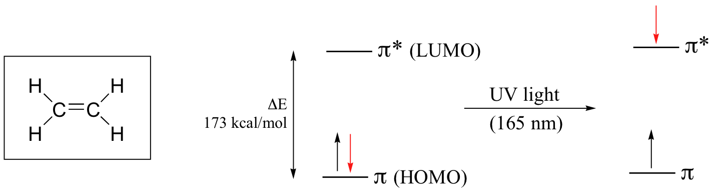
Electronic transitions

Let's take as our first example the simple case of molecular hydrogen, H_2. As you may recall from section 2.1A, the molecular orbital picture for the hydrogen molecule consists of one bonding σ MO, and a higher energy antibonding σ* MO. When the molecule is in the ground state, both electrons are paired in the lower-energy bonding orbital – this is the Highest Occupied Molecular Orbital (HOMO). The antibonding σ* orbital, in turn, is the Lowest Unoccupied Molecular Orbital (LUMO).



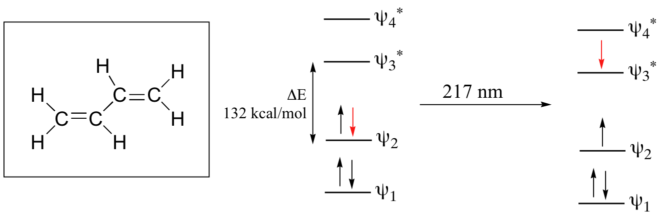
If the molecule is exposed to light of a wavelength with energy equal to **Δ**E, the HOMO-LUMO energy gap, this wavelength will be absorbed and the energy used to bump one of the electrons from the HOMO to the LUMO – in other words, from the σ to the σ* orbital. This is referred to as a **σ - σ* transition**. **Δ**E for this electronic transition is 258 kcal/mol, corresponding to light with a wavelength of 111 nm.

When a double-bonded molecule such as ethene (common name ethylene) absorbs light, it undergoes a **π - π* transition.** Because π- π* energy gaps are narrower than σ **-** σ***** gaps, ethene absorbs light at 165 nm - a longer wavelength than molecular hydrogen.



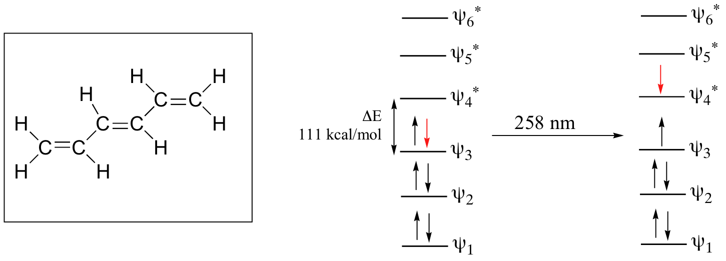
The electronic transitions of both molecular hydrogen and ethene are too energetic to be accurately recorded by standard UV spectrophotometers, which generally have a range of 220 – 700 nm. Where UV-vis spectroscopy becomes useful to most organic and biological chemists is in the study of molecules with conjugated *π* systems. In these groups, the energy gap for π -*π** transitions is smaller than for isolated double bonds, and thus the wavelength absorbed is longer. Molecules or parts of molecules that absorb light strongly in the UV-vis region are called **chromophores**.

Let's revisit the MO picture for 1,3-butadiene, the simplest conjugated system. Recall that we can draw a diagram showing the four pi MO's that result from combining the four $2p_z$ atomic orbitals. The lower two orbitals are bonding, while the upper two are antibonding.

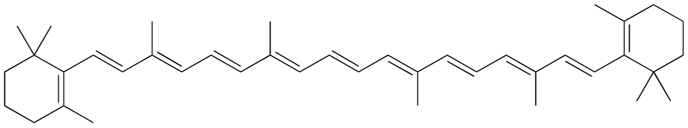


Comparing this MO picture to that of ethene, our isolated pi-bond example, we see that the HOMO-LUMO energy gap is indeed smaller for the conjugated system. 1,3-butadiene absorbs UV light with a wavelength of 217 nm.

As conjugated pi systems become larger, the energy gap for a π - π* transition becomes increasingly narrow, and the wavelength of light absorbed correspondingly becomes longer. The absorbance due to the π - π* transition in 1,3,5-hexatriene, for example, occurs at 258 nm, corresponding to a **Δ**E of 111 kcal/mol.

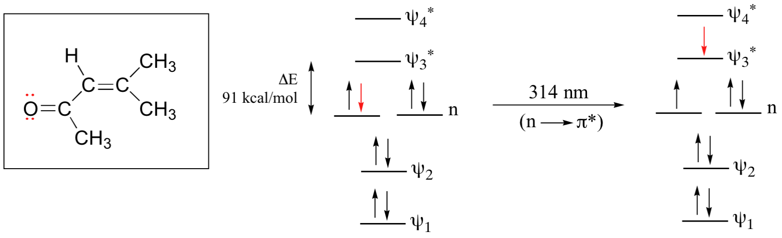


In molecules with extended pi systems, the HOMO-LUMO energy gap becomes so small that absorption occurs in the visible rather then the UV region of the electromagnetic spectrum. Beta-carotene, with its system of 11 conjugated double bonds, absorbs light with wavelengths in the blue region of the visible spectrum while allowing other visible wavelengths – mainly those in the red-yellow region - to be transmitted. This is why carrots are orange.



β-carotene

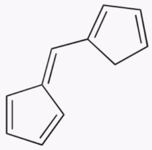
The conjugated pi system in 4-methyl-3-penten-2-one gives rise to a strong UV absorbance at 236 nm due to a π - π* transition. However, this molecule also absorbs at 314 nm. This second absorbance is due to the transition of a non-bonding (lone pair) electron on the oxygen up to a π* antibonding MO:



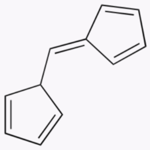
This is referred to as an **n - π* transition**. The nonbonding (n) MO's are higher in energy than the highest bonding p orbitals, so the energy gap for an $n \rightarrow \pi^*$ transition is smaller that that of a π - π* transition – and thus the n - π* peak is at a longer wavelength. In general, n - π* transitions are weaker (less light absorbed) than those due to π - π* transitions.

Exercise 4.9: What is the energy of the photons (in kJ/mol) of light with wavelength of 470 nm, the l_{max} of b-carotene?

Exercise 4.10: Which of the following molecules would you expect absorb at a longer wavelength in the UV region of the electromagnetic spectrum? Explain your answer.



A

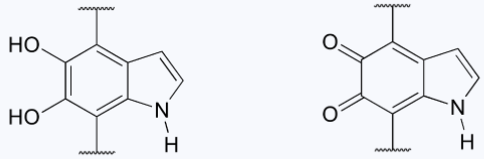


B

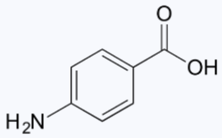
Solutions

Protecting yourself from sunburn

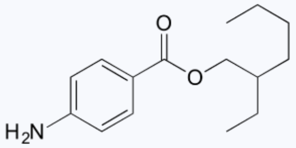
Human skin can be damaged by exposure to ultraviolet light from the sun. We naturally produce a pigment, called melanin, which protects the skin by absorbing much of the ultraviolet radiation. Melanin is a complex polymer, two of the most common monomers units of which are shown below.



common monomer units in melanin



PABA

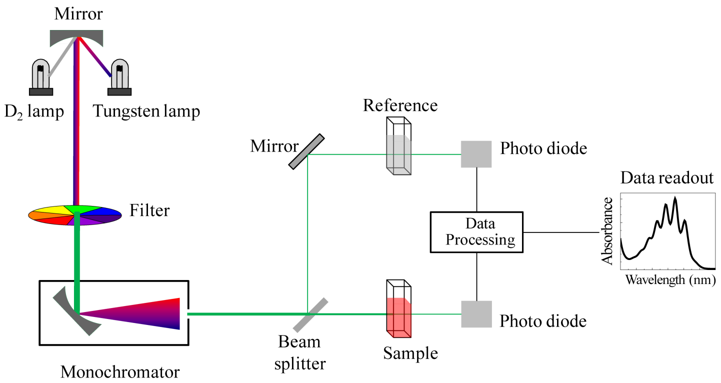


Padimate-O

Overexposure to the sun is still dangerous, because there is a limit to how much radiation our melanin can absorb. Most commercial sunscreens claim to offer additional protection from both UV-A and UV-B radiation: UV-A refers to wavelengths between 315-400 nm, UV-B to shorter, more harmful wavelengths between 280-315 nm. PABA (*para*-aminobenzoic acid) was used in sunscreens in the past, but its relatively high polarity meant that it was not very soluble in oily lotions, and it tended to rinse away when swimming. Many sunscreens today contain, among other active ingredients, a more hydrophobic derivative of PABA called Padimate O.

Looking at UV-vis spectra

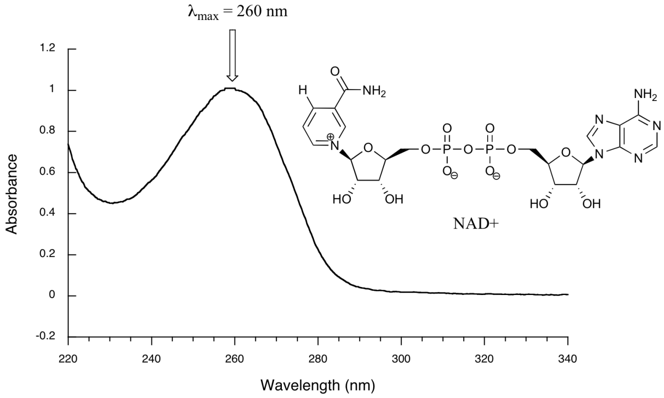
We have been talking in general terms about how molecules absorb UV and visible light – now let's look at some actual examples of data from a UV-vis absorbance spectrophotometer. The basic setup is the same as for IR spectroscopy: radiation with a range of wavelengths is directed through a sample of interest, and a detector records which wavelengths were absorbed and to what extent the absorption occurred.



Schematic for a UV-Vis spectrophotometer

(Image from Wikipedia Commons)

Below is the absorbance spectrum of an important biological molecule called nicotinamide adenine dinucleotide, abbreviated NAD$^+$. This compound absorbs light in the UV range due to the presence of conjugated pi-bonding systems.



You'll notice that this UV spectrum is much simpler than the IR spectra we saw earlier: this one has only one peak, although many molecules have more than one. Notice also that the convention in UV-vis spectroscopy is to show the baseline at the bottom of the graph with the peaks pointing up. Wavelength values on the x-axis are generally measured in nanometers (nm) rather than in cm^{-1} as is the convention in IR spectroscopy.

Peaks in UV spectra tend to be quite broad, often spanning well over 20 nm at half-maximal height. Typically, there are two things that we look for and record from a UV-Vis spectrum. The first is λ_{max}, which is the wavelength at maximal light absorbance. As you can see, NAD$^+$ has $\lambda_{max} = 260\ nm$. We also want to record how much light is absorbed at λ_{max}. Here we use a unitless number called **absorbance**, abbreviated 'A'. This contains the same information as the 'percent transmittance' number used in IR spectroscopy, just expressed in slightly different terms. To calculate absorbance at a given wavelength, the computer in the spectrophotometer simply takes the intensity of light at that wavelength *before* it passes through the sample (I_0), divides this value by the intensity of the same wavelength *after* it passes through the sample (I), then takes the $\log_{10}$ of that number:

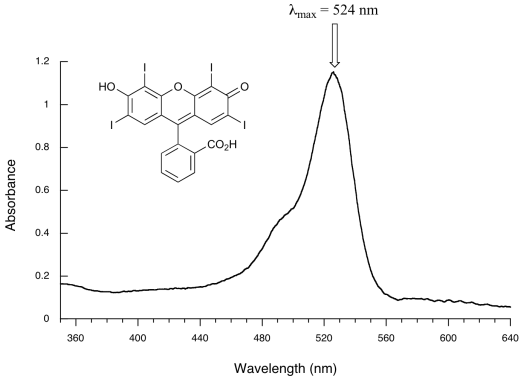
$$A = \log \frac{I_0}{I} \tag{4.3.1}$$

You can see that the absorbance value at 260 nm (A_{260}) is about 1.0 in this spectrum.

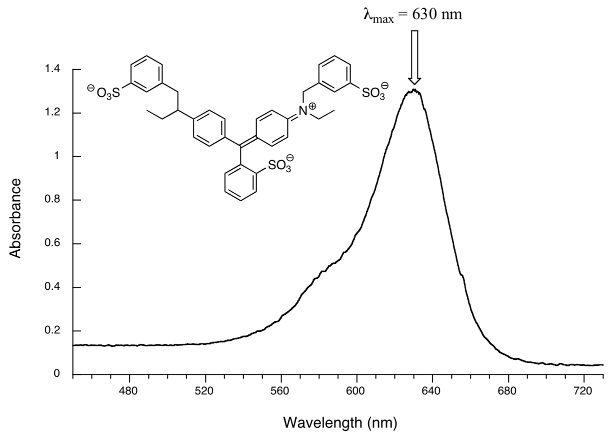
Exercise 4.11: Express A = 1.0 in terms of percent transmittance (%T, the unit usually used in IR spectroscopy (and sometimes in UV-vis as well).

Solutions

Here is the absorbance spectrum of the common food coloring Red #3:



Here, we see that the extended system of conjugated pi bonds causes the molecule to absorb light in the visible range. Because the λ_{max} of 524 nm falls within the green region of the spectrum, the compound appears red to our eyes. Now, take a look at the spectrum of another food coloring, Blue #1:



Here, maximum absorbance is at 630 nm, in the orange range of the visible spectrum, and the compound appears blue.

Applications of UV spectroscopy in organic and biological chemistry

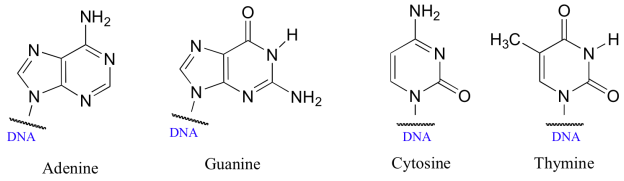
UV-vis spectroscopy has many different applications in organic and biological chemistry. One of the most basic of these applications is the use of the **Beer - Lambert Law** to determine the concentration of a chromophore. You most likely have performed a Beer – Lambert experiment in a previous chemistry lab. The law is simply an application of the observation that, within certain ranges, the absorbance of a chromophore at a given wavelength varies in a linear fashion with its concentration: the higher the concentration of the molecule, the greater its absorbance.

If we divide the observed value of A at λ_{max} by the concentration of the sample (*c*, in mol/L), we obtain the **molar absorptivity**, or **extinction coefficient** (**ε**), which is a characteristic value for a given compound.

$$\epsilon = \frac{A}{c} \tag{4.3.2}$$

The absorbance will also depend, of course, on the **path length** - in other words, the distance that the beam of light travels though the sample. In most cases, sample holders are designed so that the path length is equal to 1 cm, so the units for molar absorptivity are L$_*$ mol^{-1}$_*$cm^{-1}. If we look up the value of e for our compound at λ_{max}, and we measure absorbance at this wavelength, we can easily calculate the concentration of our sample. As an example, for NAD$^+$ the literature value of ε at 260 nm is 18,000 L$_*$ mol^{-1}$_*$cm^{-1}. In our NAD$^+$ spectrum we observed A_{260} = 1.0, so using equation 4.4 and solving for concentration we find that our sample is 5.6 x 10^{-5} M.

The bases of DNA and RNA are good chromophores:

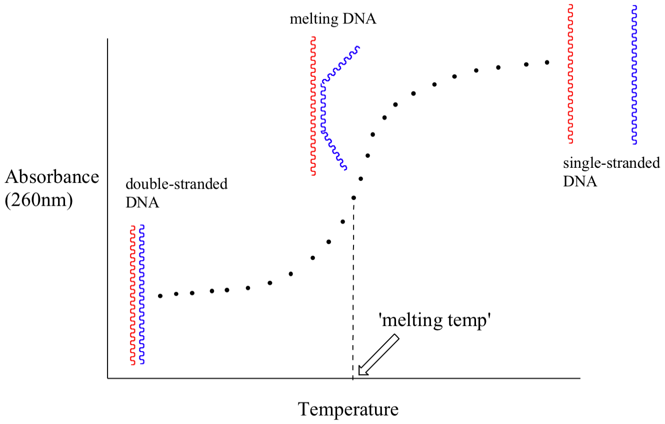


Biochemists and molecular biologists often determine the concentration of a DNA sample by assuming an average value of ε = 0.020 ng^{-1}×mL for double-stranded DNA at its λ_{max} of 260 nm (notice that concentration in this application is expressed in mass/volume rather than molarity: ng/mL is often a convenient unit for DNA concentration when doing molecular biology).

Exercise 4.12: 50 microliters of an aqueous sample of double stranded DNA is dissolved in 950 microliters of water. This diluted solution has a maximal absorbance of 0.326 at 260 nm. What is the concentration of the original (more concentrated) DNA sample, expressed in micrograms per microliter?

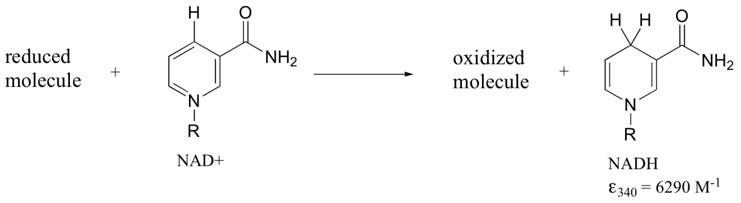
Solutions

Because the extinction coefficient of double stranded DNA is slightly lower than that of single stranded DNA, we can use UV spectroscopy to monitor a process known as DNA melting. If a short stretch of double stranded DNA is gradually heated up, it will begin to ‘melt’, or break apart, as the temperature increases (recall that two strands of DNA are held together by a specific pattern of hydrogen bonds formed by ‘base-pairing’).

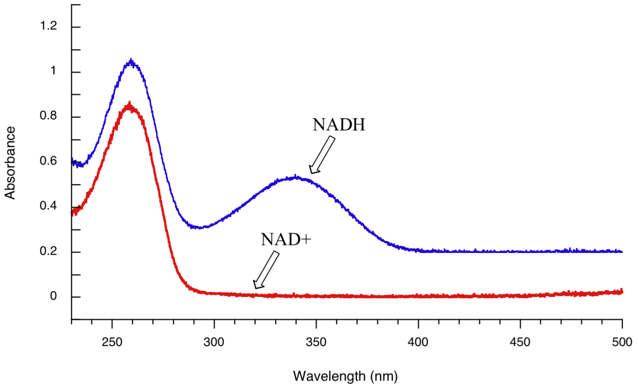


As melting proceeds, the absorbance value for the sample increases, eventually reaching a high plateau as all of the double-stranded DNA breaks apart, or ‘melts’. The mid-point of this process, called the ‘melting temperature’, provides a good indication of how tightly the two strands of DNA are able to bind to each other.

Later we will see how the Beer - Lambert Law and UV spectroscopy provides us with a convenient way to follow the progress of many different enzymatic redox (oxidation-reduction) reactions. In biochemistry, oxidation of an organic molecule often occurs concurrently with reduction of nicotinamide adenine dinucleotide (NAD^+, the compound whose spectrum we saw earlier in this section) to NADH:

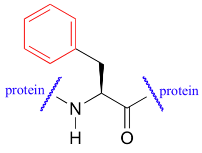


Both NAD^+ and NADH absorb at 260 nm. However NADH, unlike NAD^+, has a second absorbance band with λ_{max} = 340 nm and ε = 6290 $L{*}mol^{-1}{*}cm^{-1}$. The figure below shows the spectra of both compounds superimposed, with the NADH spectrum offset slightly on the y-axis:

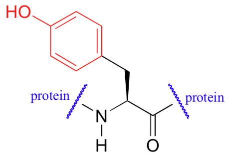


By monitoring the absorbance of a reaction mixture at 340 nm, we can 'watch' NADH being formed as the reaction proceeds, and calculate the rate of the reaction.

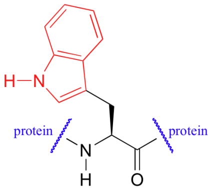
UV spectroscopy is also very useful in the study of proteins. Proteins absorb light in the UV range due to the presence of the aromatic amino acids tryptophan, phenylalanine, and tyrosine, all of which are chromophores.



phenylalanine



tyrosine



tryptophan

Biochemists frequently use UV spectroscopy to study conformational changes in proteins - how they change shape in response to different conditions. When a protein undergoes a conformational shift (partial unfolding, for example), the resulting change in the environment around an aromatic amino acid chromophore can cause its UV spectrum to be altered.

Kahn Academy video tutorials on UV-Vis spectroscopy

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

20.4: Nuclear Magnetic Resonance Spectroscopy

20.5: Introduction to Atmospheric Photochemistry

20.6: Photosynthesis

SECTION OVERVIEW

Unit 6: Materials

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

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XVII XVIII XIX XX XXI XXII XXIII • **Homework Exercises**

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21: Structure and Bonding in Solids

22: Inorganic Materials

23: Polymeric Materials and Soft Condensed Matter

CHAPTER OVERVIEW

21: Structure and Bonding in Solids

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Principles of Modern Chemistry

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I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI XVII XVIII XIX XX XXI XXII XXIII • **Homework Exercises**

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21.1: Crystal Symmetry and the Unit Cell

21.2: Crystal Structure

21.3: Cohesion in Solids

21.4: Defects and Amorphous Solids

Discussion Questions

- What are crystal defects and how are they classified?
- How do impurities affect the structure and properties of a solid?
- What are color centers and how do they affect electric conductivity of solids?

Few, if any, crystals are *perfect* in that all unit cells consist of the ideal arrangement of atoms or molecules and all cells line up in a three dimensional space with no distortion. Some cells may have one or more atoms less whereas others may have one or more atoms than the ideal unit cell. The imperfection of crystals are called **crystal defects**. Crystal defects are results of thermodynamic equilibrium contributed also by the increase in entropy *TS* term of the Gibb's free energy:

$$\Delta G = \Delta H - T \Delta S$$

Only at the unattainable absolute zero K will a crystal be perfect, in other words, no crystals are absolutely perfect. However, the degree of imperfection vary from compound to compound. On the other hand, some solid-like structure called **flickering clusters** also exist in a liquid. For example, the density of water is the highest at 277 K. The flickering clusters increase as temperature drops below 277 K, and the water density decreases as a result. The missing and lacking of atoms or ions in an ideal or imaginary crystal structure or lattice and the misalignment of unit cells in real crystals are called crystal defects or solid defects. Crystal defects occur as points, along lines, or in the form of a surface, and they are called **point, line, or plane defects** respectively.

Point Defects

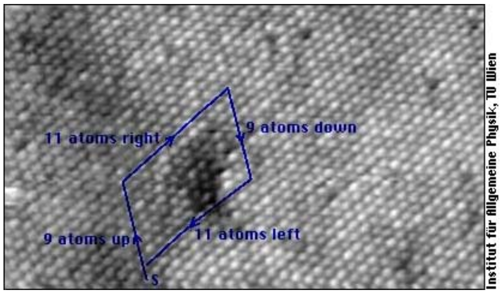
Point defects can be divided into Frenkel defects and **Schottky defects**, and these often occur in ionic crystals. The former are due to misplacement of ions and vacancies. Charges are balanced in the whole crystal despite the presence of interstitial or extra ions and vacancies. On the other hand, when only vacancies of cation and anions are present with no interstitial or misplaced ions, the defects are called Schottky defects.

Point defects are common in crystals with large anions such as AgBr, AgI, $RbAgI_4$. Due to the defects, the ions have some freedom to move about in crystals, making them relatively good conductors. These are called ionic conductors, unlike metals in which electrons are responsible for electric conductivity. Recently, ionic conductors have attracted a lot of attention because the fuel cell and battery technologies require conducting solids to separate the electrodes.

Line Defects

Line defects are mostly due to misalignment of ions or presence of vacancies along a line. When lines of ions are missing in an otherwise perfect array of ions, an **edge dislocation** appeared. Edge dislocation is responsible for the ductility and malleability. In fact the hammering and stretching of materials often involve the movement of edge dislocation. Movements of dislocations give rise to their plastic behavior. Line dislocations usually do not end inside the crystal, and they either form loops or end at the surface of a single crystal.

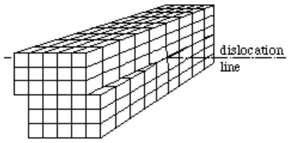
A dislocation is characterized by its Burgers vector: If you imagine going around the dislocation line, and exactly going back as many atoms in each direction as you have gone forward, you will not come back to the same atom where you have started. The Burgers vector points from start atom to the end atom of your journey (This "journey" is called Burgers circuit in dislocation theory).



Institut für Allgemeine Physik, TU Wien

In this electron microscope image of the surface of a crystal, you see point defects and a Burger journey around an edge dislocation. The dislocation line is in the crystal, and the image shows its ending at the surface. A Burger vector is approximately perpendicular to the dislocation line, and the missing line of atoms is somewhere within the block of the Buerger journey.

If the misalignment shifts a block of ions gradually downwards or upwards causing the formation of a screw like deformation, a **screw dislocation** is formed. The diagram here shows the idealized screw dislocation.



Line defects weakens the structure along a one-dimensional space, and the defects type and density affects the mechanical properties of the solids. Thus, formation and study of dislocations are particularly important for structural materials such as metals. This link gives some impressive images of dislocations. Chemical etching often reveal pits which are visible under small magnifications.

✓ Example 21.4.1

The Table of X-ray Crystallographic Data of Minerals (The CRC Handbook of Chemistry and Physics) list the following for bunsenite (NiO): Crystal system: cubic, structure type: rock salt, a = 4.177*10-8 cm. In the table of Physical Constant of Inorganic Compounds, the density of bunsenite (NiO) is 6.67g / cm3. From these values, evaluate the cell volume (volume of the unit cell), sum of Ni and O radii (rNi + rO), 2 Molar volumes, (X-ray) density, and the Schottky defect vacancy rate.

Solution
Actually, most of the required values have been listed in the table, but their evaluations illustrate the methods. These values are evaluated below:

Cell volume = a3
= (4.177*10-8)3
= 72.88*10-24 cm3

$$r_{Ni} + r_O = \frac{a}{2}$$

$$= 2.088 \times 10^{-8}$$

X-ray density = 4*(58.69+16.00) / (6.023*10^{23}*72.88*10^{-24})
= 6.806 g / cm^3,

Compared to the observed density = 6.67 g / cm^3. The molar volumes (58.69+16.00) / density are thus

74.69 / 6.806 = 10.97 cm^3; and 74.69 / 6.67 = 11.20 cm^3

The vacancy rate = 6.806 - 6.67 / 6.806
= 0.02 (or 2%)

DISCUSSION

These methods are hints to assignments.

From the given conditions, we cannot calculate individual radii of Ni and O, but their sum is calculable.

Plane Defects

Plane defects occur along a 2-dimensional surface. The **surface** of a crystal is an obvious imperfection, because these surface atoms are different from those deep in the crystals. When a solid is used as a catalyst, the catalytic activity depends very much on the surface area per unit mass of the sample. For these powdery material, methods have been developed for the determination of unit areas per unit mass.

Another surface defects are along the **grain boundaries**. A grain is a single crystal. If many seeds are formed when a sample starts to crystallize, each seed grow until they meet at the boundaries. Properties along these boundaries are different from the grains. A third plane defects are the **stacking faults**. For example, in the close packing arrangement, the adjancent layers always have the AB relationship. In a ccp (fcc) close packing sequence, ...ABCABC..., one of the layer may suddenly be out of sequence, and become ..ABABCABC.... Similarly, in the hcp sequence, there is a possibility that one of the layer accidentally startes in the C location and resulting in the formation of a grain boundary.

How do impurities affect the structure and properties of a solid?

You already know that to obtain a perfectly pure substance is almost impossible. Purification is a costly process. In general, analytical reagent-grade chemicals are of high purity, and yet few of them are better than 99.9% pure. This means that a foreign atom or molecule is present for every 1000 host atoms or molecules in the crystal. Perhaps the most demanding of purity is in the electronic industry. Silicon crystals of 99.999 (called 5 nines) or better are required for IC chips productions. These crystal are **doped** with nitrogen group elements of P and As or boron group elements B, Al etc to form n- aand p-type semiconductors. In these crystals, the impurity atom substitute atoms of the host crystals.

Presence minute foreign atoms with one electron more or less than the valence four silicon and germanium host atoms is the key of making n- and p-type semiconductors. Having many semiconductors connected in a single chip makes the integrated circuit a very efficient information processor. The electronic properties change dramatically due to these impurities. This is further described in Inorganic Chemistry by Swaddle.

In other bulk materials, the presence of impurity usually leads to a lowering of melting point. For example, Hall and Heroult tried to electrolyze natural aluminum compounds. They discovered that using a 5% mixture of Al_2O_3 (melting point 273 K) in cryolite Na_3AlF_6 (melting point 1273 K) reduced the melting point to 1223 K, and that enabled the production of aluminum in bulk. Recent modifications lowered melting temperatures below 933 K. Some types of glass are made by mixing silica (SiO_2), alumina (Al_2O_3), calcium oxide (CaO), and sodium oxide (Na_2O). They are softer, but due to lower melting points, they are cheaper to produce.

Color centers and how do they affect electric conductivity of solids?

Color centers are imperfections in crystals that cause color (defects that cause color by absorption of light). Due to defects, metal oxides may also act as semiconductors, because there are many different types of electron traps. Electrons in defect region only absorb light at certain range of wavelength. The color seen are due to lights not absorbed. For example, a diamond with C vacancies (missing carbon atoms) absorbs light, and these centers give green color as shown here. Replacement of Al^{3+} for Si^{4+} in quartz give rise to the color of smoky quartz.

A high temperature phase of ZnO_x, ($x < 1$), has electrons in place of the O^{2-} vacancies. These electrons are color centers, often referred to as *F*-centers (from the German word *farben* meaning color). Similarly, heating of ZnS to 773 K causes a loss of sulfur, and these material fluoresces strongly in ultraviolet light. Some non-stoichiometric solids are engineered to be n-type or p-type semiconductors. Nickel oxide NiO gain oxygen on heating in air, resulting in having Ni^{3+} sites acting as electron trap, a p-type semiconductor. On the other hand, ZnO lose oxygen on heating, and the excess Zn metal atoms in the sample are ready to give electrons. The solid is an n-type semiconductor.

Questions

1. Why does the density of water decreases when the temperature decreases from 277 to 273 K?
2. What type of defects is due to misplaced atoms or ions and vacancies of the same in a crystalline material.
3. What defects reduce the density of a solid?
4. What type of material do the fuel cell and battery technologies need to separate the electrodes?

Solutions

1. **Hint: Due to the formation of flickering clusters.**

   Skill -
   Correlate properties of a material to its structure.

2. **Hint: Frenkel defects.**

   Skill -
   Explain Frendel and Schottky defects.

3. **Hint: Vacancies of Schottky defects reduce the density.**

   Skill -
   Correlate properties of a material to its structure.

4. **Hint: Ionic conductors.**

   Skill -
   Specify the desirable properties of a material.

Contributors and Attributions

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21.5: Lattice Energies of Crystals

Learning Objectives

- To understand the relationship between the lattice energy and physical properties of an ionic compound.
- To use the Born–Haber cycle to calculate lattice energies.

Recall that the reaction of a metal with a nonmetal usually produces an ionic compound; that is, electrons are transferred from the metal (the *reductant*) to the nonmetal (the *oxidant*). Ionic compounds are usually rigid, brittle, crystalline substances with flat surfaces that intersect at characteristic angles. They are not easily deformed, and they melt at relatively high temperatures. NaCl, for example, melts at 801°C. These properties result from the regular arrangement of the ions in the crystalline lattice and from the strong electrostatic attractive forces between ions with opposite charges.

While formation of ion pairs from isolated ions releases large amounts of energy, even more energy is released when these ion pairs condense to form an ordered three-dimensional array. In such an arrangement each cation in the lattice is surrounded by more than one anion (typically four, six, or eight) and vice versa, so it is more stable than a system consisting of separate pairs of ions, in which there is only one cation–anion interaction in each pair. Note that r_0 may differ between the gas-phase dimer and the lattice.

> An ionic lattice is more stable than a system consisting of separate ion pairs.

Calculating (Ionic) Lattice Energies

The lattice energy of nearly any ionic solid can be calculated rather accurately using a modified form of **Coulomb's law**:

$$U = -\frac{k'Q_1Q_2}{r_0} \tag{21.5.1}$$

where U, which is always a positive number, represents the amount of energy required to dissociate 1 mol of an ionic solid into the gaseous ions. The proportionality constant in Equation 21.5.1 is expanded below, but it is worthwhile to discuss its general features first.

If we assume that $\Delta V = 0$, then the lattice energy, U, is approximately equal to the change in enthalpy, ΔH:

$$\mathrm{MX(s) \rightarrow M^{+n}(g) + X^{-n}(g)} \qquad \Delta H \approx U \tag{21.5.2}$$

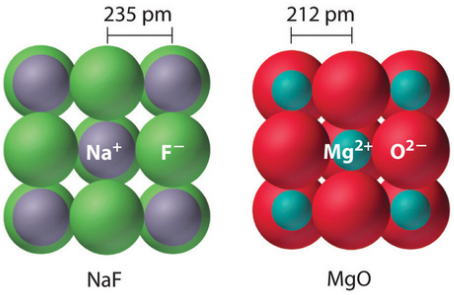
As before, Q_1 and Q_2 are the charges on the ions and r_0 is the internuclear distance. We see from Equation 21.5.1 that lattice energy is directly related to the product of the ion charges and inversely related to the internuclear distance. The value of the constant k' depends on the specific arrangement of ions in the solid lattice and their valence electron configurations. Representative values for calculated lattice energies, which range from about 600 to 10,000 kJ/mol, are listed in Table $21.5.1$. Energies of this magnitude can be decisive in determining the chemistry of the elements.

Table 21.5.1: Representative Calculated Lattice Energies

Substance	U (kJ/mol)
NaI	682
CaI_2	1971
MgI_2	2293
NaOH	887
Na_2O	2481
$NaNO_3$	755
$Ca_3(PO_4)_2$	10,602
$CaCO_3$	2804

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Because the lattice energy depends on the *product* of the charges of the ions, a salt having a metal cation with a +2 charge (M^{2+}) and a nonmetal anion with a −2 charge (X^{2-}) will have a lattice energy four times greater than one with M^+ and X^-, assuming the ions are of comparable size (and have similar internuclear distances). For example, the calculated value of U for NaF is 910 kJ/mol, whereas U for MgO (containing Mg^{2+} and O^{2-} ions) is 3795 kJ/mol.



Because lattice energy is *inversely* related to the internuclear distance, it is also inversely proportional to the size of the ions. This effect is illustrated in Figure 21.5.1, which shows that lattice energy decreases for the series LiX, NaX, and KX as the radius of X^- increases. Because r_0 in Equation 21.5.1 is the sum of the ionic radii of the cation and the anion ($r_0 = r^+ + r^-$), r_0 increases as the cation becomes larger in the series, so the magnitude of U decreases. A similar effect is seen when the anion becomes larger in a series of compounds with the same cation.

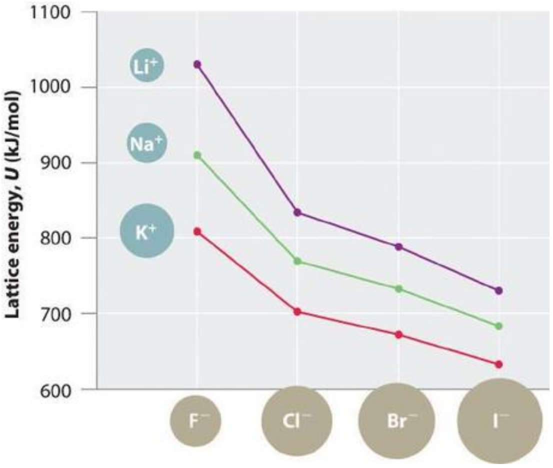


Figure 21.5.1: A Plot of Lattice Energy versus the Identity of the Halide for the Lithium, Sodium, and Potassium Halides

Because the ionic radii of the cations decrease in the order $K^+ > Na^+ > Li^+$ for a given halide ion, the lattice energy decreases smoothly from Li^+ to K^+. Conversely, for a given alkali metal ion, the fluoride salt always has the highest lattice energy and the iodide salt the lowest.

> *Lattice energies are highest for substances with small, highly charged ions.*

✓ Example 21.5.1

Arrange GaP, BaS, CaO, and RbCl in order of increasing lattice energy.

Given: four compounds

Asked for: order of increasing lattice energy

Strategy:

Using Equation 21.5.1, predict the order of the lattice energies based on the charges on the ions. For compounds with ions with the same charge, use the relative sizes of the ions to make this prediction.

Solution:

The compound GaP, which is used in semiconductor electronics, contains Ga^{3+} and P^{3-} ions; the compound BaS contains Ba^{2+} and S^{2-} ions; the compound CaO contains Ca^{2+} and O^{2-} ions; and the compound RbCl has Rb^+ and Cl^- ions. We know from

Equation 21.5.1 that lattice energy is directly proportional to the product of the ionic charges. Consequently, we expect RbCl, with a (−1)(+1) term in the numerator, to have the lowest lattice energy, and GaP, with a (+3)(−3) term, the highest. To decide whether BaS or CaO has the greater lattice energy, we need to consider the relative sizes of the ions because both compounds contain a +2 metal ion and a −2 chalcogenide ion. Because Ba^{2+} lies below Ca^{2+} in the periodic table, Ba^{2+} is larger than Ca^{2+}. Similarly, S^{2-} is larger than O^{2-}. Because the cation and the anion in BaS are both larger than the corresponding ions in CaO, the internuclear distance is greater in BaS and its lattice energy will be lower than that of CaO. The order of increasing lattice energy is RbCl < BaS < CaO < GaP.

Exercise 21.5.1

Arrange InAs, KBr, LiCl, SrSe, and ZnS in order of decreasing lattice energy.

Answer

InAs > ZnS > SrSe > LiCl > KBr

Lattice Energy also Depends on Crystal Structure

There are many other factors to be considered such as covalent character and electron-electron interactions in ionic solids. But for simplicity, let us consider the ionic solids as a collection of positive and negative ions. In this simple view, appropriate number of cations and anions come together to form a solid. The positive ions experience both attraction and repulsion from ions of opposite charge and ions of the same charge.

As an example, let us consider the the NaCl crystal. In the following discussion, assume *r* be the distance between Na^+ and Cl^- ions. The nearest neighbors of Na^+ are 6 Cl^- ions at a distance 1*r*, 12 Na^+ ions at a distance 2*r*, 8 Cl^- at 3*r*, 6 Na^+ at 4*r*, 24 Na^+ at 5*r*, and so on. Thus, the electrostatic potential of a single ion in a crystal by approximating the ions by point charges of the surrounding ions:

$$E_{ion-lattice} = \frac{Z^2e^2}{4\pi\epsilon_o r}M \tag{21.5.3}$$

The Madelung constant M - named after Erwin Medelung - is a geometrical factor that depends on the arrangement of ions in the solid. For example, M for NaCl is a poorly converging series of interaction energies:

$$M = \frac{6}{1} - \frac{12}{2} + \frac{8}{3} - \frac{6}{4} + \frac{24}{5}\ldots \tag{21.5.4}$$

with

- Z is the number of charges of the ions, (e.g., 1 for NaCl),
- e is the charge of an electron ($1.6022 \times 10^{-19}\ C$),
- $4\pi\epsilon_o$ is 1.11265x10^{-10} C^2/(J m).

The Madelung constant depends on the structure type and Equation 21.5.4 is applicable only for the sodium chloride (e.g., rock salt) lattice geometry. Other values for other structural types are given in Table $21.5.2$

Table 21.5.2: Madelung Constants. *A* is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion.

Compound	Crystal Lattice	M	A : C	Type
NaCl	NaCl	1.74756	6 : 6	Rock salt
CsCl	CsCl	1.76267	6 : 6	CsCl type
CaF_2	Cubic	2.51939	8 : 4	Fluorite
$CdCl_2$	Hexagonal	2.244		
MgF_2	Tetragonal	2.381		
ZnS (wurtzite)	Hexagonal	1.64132		
TiO_2 (rutile)	Tetragonal	2.408	6 : 3	Rutile

Compound	Crystal Lattice	M	A : C	Type
bSiO$_2$	Hexagonal	2.2197		
Al$_2$O$_3$	Rhombohedral	4.1719	6 : 4	Corundum

There are other factors to consider for the evaluation of lattice energy and the treatment by Max Born and Alfred Landé led to the formula for the evaluation of lattice energy for a mole of **crystalline solid**. The Born–Landé equation (Equation 21.5.5) is a means of calculating the lattice energy of a crystalline ionic compound and derived from the electrostatic potential of the ionic lattice and a repulsive potential energy term

$$U = \frac{N_A M z^+ z^- e^2}{4\pi\epsilon_o r_o}\left(1 - \frac{1}{n}\right) \tag{21.5.5}$$

where

- N_A is Avogadro constant
- M is the Madelung constant for the lattice
- z^+ is the charge number of cation
- z^- is the charge number of anion
- e is elementary charge ($1.6022 \times 10^{-19} C$)
- ε_0 is the permittivity of free space ($8.854 \times 10^{-12} C^2/m$)
- r_0 is the distance to closest ion
- n is the **Born exponent** that is typically between 5 and 12 and is determined experimentally. n is a number related to the electronic configurations of the ions involved (Table $21.5.3$).

Table 21.5.3: n values for select solids

Atom/Molecule	*n*
He	5
Ne	7
Ar	9
Kr	10
Xe	12
LiF	5.9
LiCl	8.0
LiBr	8.7
NaCl	9.1
NaBr	9.5

✓ Example 21.5.2

Estimate the lattice energy for $NaCl$·

Solution

Using the values giving in the discussion above, the estimation is given by Equation 21.5.5

$$\begin{aligned} U_{NaCl} &= \frac{(6.022 \times 10^{23}/mol)(1.74756)(1)(1)(1.6022 \times 10^{-19}\ C)^2}{4\pi\,(8.854 \times 10^{-12} C^2/m)(282 \times 10^{-12}\ m)}\left(1 - \frac{1}{9.1}\right) \\ &= -756\ kJ/mol \end{aligned}$$

Discussion

> Much more should be considered in order to evaluate the lattice energy accurately, but the above calculation leads you to a good start. When methods to evaluate the energy of crystallization or lattice energy lead to reliable values, these values can be used in the Born-Hable cycle to evaluate other chemical properties, for example the electron affinity, which is really difficult to determine directly by experiment.

The Relationship between Lattice Energies and Physical Properties

The magnitude of the forces that hold an ionic substance together has a dramatic effect on many of its properties. The melting point, for example, is the temperature at which the individual ions have enough kinetic energy to overcome the attractive forces that hold them in place. At the melting point, the ions can move freely, and the substance becomes a liquid. Thus melting points vary with lattice energies for ionic substances that have similar structures. The melting points of the sodium halides (Figure $21.5.2$), for example, decrease smoothly from NaF to NaI, following the same trend as seen for their lattice energies (Figure $21.5.1$). Similarly, the melting point of MgO is 2825°C, compared with 996°C for NaF, reflecting the higher lattice energies associated with higher charges on the ions. In fact, because of its high melting point, MgO is used as an electrical insulator in heating elements for electric stoves.

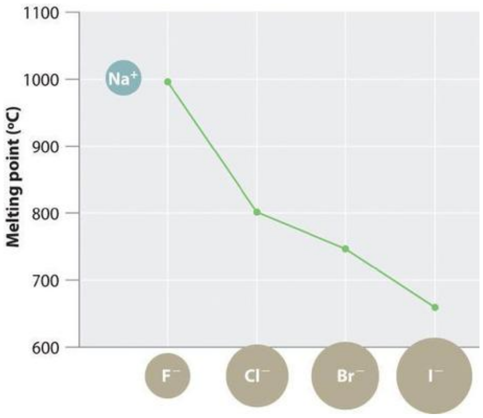


Figure 21.5.2: A Plot of Melting Point versus the Identity of the Halide for the Sodium Halides. The melting points follow the same trend as the magnitude of the lattice energies in Figure 21.5.1.

The hardness of ionic materials—that is, their resistance to scratching or abrasion—is also related to their lattice energies. Hardness is directly related to how tightly the ions are held together electrostatically, which, as we saw, is also reflected in the lattice energy. As an example, MgO is harder than NaF, which is consistent with its higher lattice energy.

In addition to determining melting point and hardness, lattice energies affect the solubilities of ionic substances in water. In general, *the higher the lattice energy, the less soluble a compound is in water*. For example, the solubility of NaF in water at 25°C is 4.13 g/100 mL, but under the same conditions, the solubility of MgO is only 0.65 mg/100 mL, meaning that it is essentially insoluble.

> *High lattice energies lead to hard, insoluble compounds with high melting points.*

The Born–Haber Cycle

In principle, lattice energies could be measured by combining gaseous cations and anions to form an ionic solid and then measuring the heat evolved. Unfortunately, measurable quantities of gaseous ions have never been obtained under conditions where heat flow can be measured. Instead, lattice energies are found using the experimentally determined enthalpy changes for other chemical processes, Hess's law, and a *thermochemical cycle* called the Born–Haber cycle. Developed by Max Born and Fritz Haber in 1919, the Born–Haber cycle describes a process in which an ionic solid is conceptually formed from its component elements in a stepwise manner.

Let's use the Born–Haber cycle to determine the lattice energy of $\mathrm{CsF(s)}$. CsF is a nearly ideal ionic compound because Cs is the least electronegative element that is not radioactive and F is the most electronegative element. To construct a thermochemical cycle for the formation of CsF, we need to know its enthalpy of formation, ΔH_f, which is defined by the following chemical reaction:

$$2Cs_{(s)} + F_{2(g)} \rightarrow 2CsF_{(s)} \tag{21.5.6}$$

Because enthalpy is a state function, the overall ΔH for a series of reactions is the sum of the values of ΔH for the individual reactions. We can therefore use a thermochemical cycle to determine the enthalpy change that accompanies the formation of solid

CsF from the parent *elements* (not ions). The Born–Haber cycle for calculating the lattice energy of cesium fluoride is shown in Figure 21.5.1. This particular cycle consists of six reactions, Equation 21.5.6 plus the following five reactions:

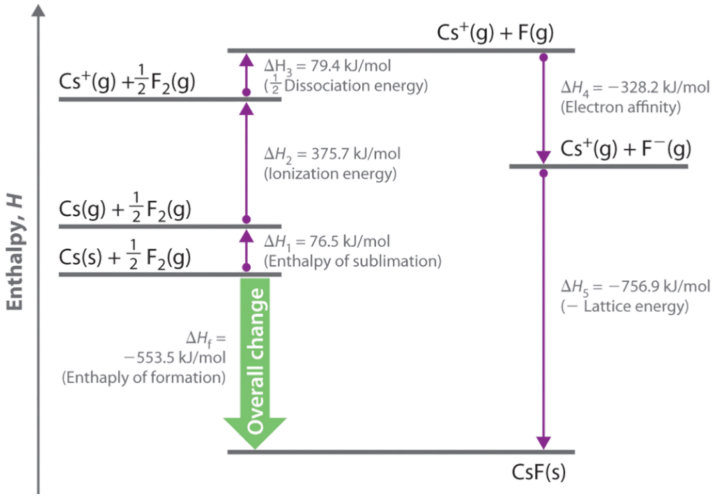


Figure 21.5.3: The Born–Haber Cycle Illustrating the Enthalpy Changes Involved in the Formation of Solid Cesium Fluoride from Its Elements

Reaction 1

$$Cs_{(s)} \rightarrow Cs_{(g)} \quad \Delta H_1 = \Delta H_{sub} = 76.5\ kJ/mol \tag{21.5.7}$$

This equation describes the sublimation of elemental cesium, the conversion of the solid directly to a gas. The accompanying enthalpy change is called the enthalpy of sublimation (ΔH_{sub}) (Table 21.5.4) and is *always* positive because energy is required to sublime a solid.

Table 21.5.4: Selected Enthalpies of Sublimation at 298 K

Substance	ΔH_{sub} (kJ/mol)
Li	159.3
Na	107.5
K	89.0
Rb	80.9
Cs	76.5
Be	324.0
Mg	147.1
Ca	177.8
Sr	164.4
Ba	180.0

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Reaction 2:

$$\mathrm{Cs(g)} \longrightarrow \mathrm{Cs^+(g)} + \mathrm{e^-} \quad \Delta H_2 = I_1 = 375.7\ kJ/mol \tag{21.5.8}$$

This equation describes the ionization of cesium, so the enthalpy change is the first ionization energy of cesium. Recall that energy is needed to ionize any neutral atom. Hence, regardless of the compound, the enthalpy change for this portion of the Born–Haber cycle is always positive.

Reaction 3:

$$\tfrac{1}{2}\mathrm{F_2(g)} \longrightarrow \mathrm{F(g)} \quad \Delta H_3 = \frac{1}{2}D = 79.4\ kJ/mol \tag{21.5.9}$$

This equation describes the dissociation of fluorine molecules into fluorine atoms, where D is the energy required for dissociation to occur (Table $21.5.5$). We need to dissociate only $\frac{1}{2}$ mol of $F_{2(g)}$ molecules to obtain 1 mol of $F_{(g)}$ atoms. The ΔH for this reaction, too, is **always** positive because energy is required to dissociate any stable diatomic molecule into the component atoms.

Table 21.5.5: Selected Bond Dissociation Enthalpies at 298 K

Substance	D (kJ/mol)
$H_2(g)$	436.0
$N_2(g)$	945.3
$O_2(g)$	498.4
$F_2(g)$	158.8
$Cl_2(g)$	242.6
$Br_2(g)$	192.8
$I_2(g)$	151.1

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Reaction 4:

$$F_{(g)} + e^- \rightarrow F^-_{(g)} \quad \Delta H_4 = EA = -328.2\ kJ/mol \tag{21.5.10}$$

This equation describes the formation of a gaseous fluoride ion from a fluorine atom; the enthalpy change is the electron affinity of fluorine. Recall that electron affinities can be positive, negative, or zero. In this case, ΔH is negative because of the highly negative electron affinity of fluorine.

Reaction 5:

$$Cs^+_{(g)} + F^-_{(g)} \rightarrow CsF_{(s)} \quad \Delta H_5 = -U \tag{21.5.11}$$

This equation describes the formation of the ionic solid from the gaseous ions. Because Reaction 5 is the reverse of the equation used to define lattice energy and U is defined to be a *positive* number, ΔH_5 is always *negative*, as it should be in a step that forms bonds.

If the enthalpy of formation of CsF from the elements is known (ΔH_f = −553.5 kJ/mol at 298 K), then the thermochemical cycle shown in Figure $21.5.3$ has only one unknown, the quantity $\Delta H_5 = -U$. From Hess's law, we can write

$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 \tag{21.5.12}$$

We can rearrange Equation 21.5.12 to give

$$-\Delta H_5 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_f \tag{21.5.13}$$

Substituting for the individual ΔHs, we obtain

$$\underbrace{U}_{-\Delta H_5} = \underbrace{\Delta H_{sub}(\mathrm{Cs})}_{\Delta H_1} + \underbrace{I_1(\mathrm{Cs})}_{\Delta H_2} + \underbrace{\frac{1}{2}D(F_2)}_{\Delta H_3} + \underbrace{EA(\mathrm{F})}_{\Delta H_4} - \underbrace{H_f(\mathrm{CsF})}_{\Delta H_f}$$

Substituting the appropriate values into this equation gives

$$\begin{aligned} U &= 76.5\ kJ/mol + 375.7\ kJ/mol + 79.4\ kJ/mol + (-328.2\ kJ/mole) - (-553.5\ kJ/mol) \\ &= 756.9\ kJ/mol \end{aligned} \tag{21.5.14}$$

U is larger in magnitude than any of the other quantities in Equation 21.5.1. The process we have used to arrive at this value is summarized in Table $21.5.6$.

Table 21.5.6: Summary of Reactions in the Born–Haber Cycle for the Formation of $\mathrm{CsF(s)}$

	Reaction	Enthalpy Change (kJ/mol)
(1)	Cs(s) → Cs(g)	$\Delta H_{sub} = 76.5$
(2)	Cs(g) → Cs + (g) + e^-	$I_1 = 375.7$
(3)	½F_2(g) → F(g)	½$D = 79.4$

(4)	$F(g) + e^- \rightarrow F^-(g)$	$EA = -328.2$
(5)	$Cs + (g) + F^-(g) \rightarrow CsF(s)$	$-U = -756.9$
total	$Cs(s) + ½F_2(g) \rightarrow CsF(s)$	$\Delta H_f = -553.5$

Predicting the Stability of Ionic Compounds

Equation 21.5.12 may be used as a tool for predicting which ionic compounds are likely to form from particular elements. As we have noted, ΔH_1 (ΔH_{sub}), ΔH_2 (I), and ΔH_3 (D) are always positive numbers, and ΔH_2 can be quite large. In contrast, ΔH_4 (EA) is comparatively small and can be positive, negative, or zero. Thus the first three terms in Equation 21.5.12 make the formation of an ionic substance energetically unfavorable, and the fourth term contributes little either way. The formation of an ionic compound will be exothermic ($\Delta H_f < 0$) if and only if ΔH_5 ($-U$) is a large negative number. This means that *lattice energy is the most important factor in determining the stability of an ionic compound*. Another example is the formation of BaO:

$$\mathrm{Ba(s)} + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{BaO(s)} \tag{21.5.15}$$

The enthalpy change is just the enthalpy of formation (e.g, $\Delta H = \Delta H_f$) with a Born–Haber cycle is compared with that for the formation of CsF in Figure 21.5.4.

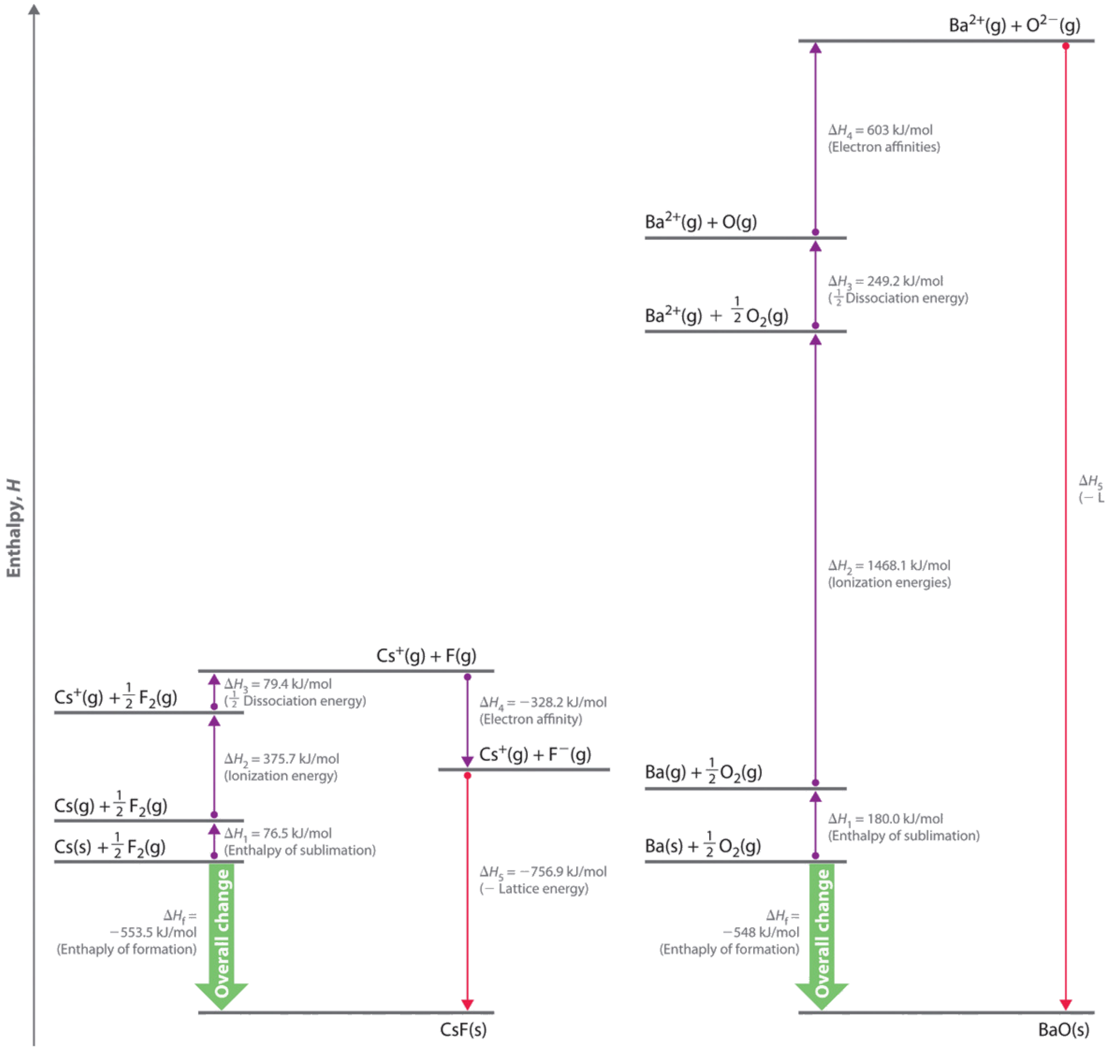


Figure 21.5.4: Comparison of the Enthalpy Changes Involved in the Formation of Solid CsF and BaO from Their Elements. (CC BY-SA-NC; anonymous)

The lattice energy of BaO, with a di-positive cation and a di-negative anion, dominates the Born–Haber cycle.

- *Reaction 1:*

$$Ba_{(s)} \rightarrow Ba_{(g)} \quad \Delta H_1 = \Delta H_{sub} = 180.0\ kJ/mol \tag{21.5.16}$$

  More than twice as much energy is required to sublime barium metal (180.0 kJ/mol) as is required to sublime cesium (76.5 kJ/mol).
- *Reaction 2:*

$$Ba_{(s)} \rightarrow Ba^{2+}_{(g)} + 2e^{-} \quad \Delta H_2 = I_1 + I_2 = 1468.1\ kJ/mol \tag{21.5.17}$$

  Nearly four times the energy is needed to form Ba^{2+} ions (I_1 = 502.9 kJ/mol, I_2 = 965.2 kJ/mol, I_1 + I_2 = 1468.1 kJ/mol) as Cs^+ ions (I_1 = 375.7 kJ/mol).
- *Reaction 3:*

$$\frac{1}{2} O_{2(g)} \rightarrow O(g) \quad \Delta H_3 = \frac{1}{2} D = 249.2\ kJ/mol \tag{21.5.18}$$

  Because the bond energy of O_2(g) is 498.4 kJ/mol compared with 158.8 kJ/mol for F_2(g), more than three times the energy is needed to form oxygen atoms from O_2 molecules as is required to form fluorine atoms from F_2.
- *Reaction 4:*

$$O_{(g)} + 2e^{-} \rightarrow O^{2-}_{(g)} \quad \Delta H_4 = EA_1 + EA_2 = 603\ kJ/mol \tag{21.5.19}$$

Forming gaseous oxide (O^{2-}) ions is energetically unfavorable. Even though adding one electron to an oxygen atom is exothermic (EA_1 = −141 kJ/mol), adding a second electron to an O^-(g) ion is energetically unfavorable (EA_2 = +744 kJ/mol)—so much so that the overall cost of forming O^{2-}(g) from O(g) is energetically prohibitive ($EA_1 + EA_2$ = +603 kJ/mol). If the first four terms in the Born–Haber cycle are all substantially more positive for BaO than for CsF, why does BaO even form? The answer is the formation of the ionic solid from the gaseous ions (Reaction 5):

- *Reaction 5:*

$$Ba^{2+}_{(g)} + O^{2-}_{(g)} \rightarrow BaO_{(s)} \quad \Delta H_5 =-U \tag{21.5.20}$$

Remember from Equations 21.5.1 and 21.5.5 that lattice energies are directly proportional to the product of the charges on the ions and inversely proportional to the internuclear distance. Although the internuclear distances are not significantly different for BaO and CsF (275 and 300 pm, respectively), the larger ionic charges in BaO produce a much higher lattice energy. Substituting values for BaO (ΔH_f = −548.0 kJ/mol) into the equation and solving for U gives:

$$\begin{aligned} U &= \Delta H_{sub}(Ba) + [I_1(Ba) + I_2(Ba)] + \frac{1}{2}D(O_2) + [EA_1(O) + EA_2(O)] - \Delta H_f(BaO) \\ &= 180.0\ kJ/mol + 1468.1\ kJ/mol + 249.2\ kJ/mol + 603\ kJ/mol - (-548.0\ kJ/mol) \\ &= 3048\ kJ/mol \end{aligned}$$

If the formation of ionic lattices containing multiple charged ions is so energetically favorable, why does CsF contain Cs^+ and F^- ions rather than Cs^{2+} and F^{2-} ions? If we assume that U for a $Cs^{2+}F^{2-}$ salt would be approximately the same as U for BaO, the formation of a lattice containing Cs^{2+} and F^{2-} ions would release 2291 kJ/mol (3048 kJ/mol − 756.9 kJ/mol) more energy than one containing Cs^+ and F^- ions. To form the Cs^{2+} ion from Cs^+, however, would require removing a 5*p* electron from a filled inner shell, which calls for a great deal of energy: I_2 = 2234.4 kJ/mol for Cs. Furthermore, forming an F^{2-} ion is expected to be even more energetically unfavorable than forming an O^{2-} ion. Not only is an electron being added to an already negatively charged ion, but because the F^- ion has a filled 2*p* subshell, the added electron would have to occupy an empty high-energy 3*s* orbital. Cesium fluoride, therefore, is not $Cs^{2+}F^{2-}$ because the energy cost of forming the doubly charged ions would be greater than the additional lattice energy that would be gained.

> *Lattice energy is usually the most important energy factor in determining the stability of an ionic compound.*

✓ Example 21.5.3

Use the thermodynamics data in the reference tables to calculate the lattice energy of MgH_2.

Given: chemical compound and data from figures and tables

Asked for: lattice energy

Strategy:

A Write a series of stepwise reactions for forming MgH_2 from its elements via the gaseous ions.

B Use Hess's law and data from the specified figures above and tables to calculate the lattice energy.

Solution:

A Hess's law allows us to use a thermochemical cycle (the Born–Haber cycle) to calculate the lattice energy for a given compound. We begin by writing reactions in which we form the component ions from the elements in a stepwise manner and then assemble the ionic solid:

(1)	$Mg_{(s)} \rightarrow Mg_{(g)}$	$\Delta H_1 =$	$\Delta H = \Delta H_{sub}(Mg)$
(2)	$Mg_{(g)} \rightarrow Mg^{2+}_{(g)} + 2e^-$	$\Delta H_2 =$	$I_1(Mg) + I_2(Mg$
(3)	$H_{2(g)} \rightarrow 2H_{(g)}$	$\Delta H_3 =$	$D(H_2)$
(4)	$2H(g) + 2e^- \rightarrow 2H^-_{(g)}$	$\Delta H_4 =$	$2EA(H)$
(5)	$Mg2+(g) + 2H^-_{(g)} \rightarrow MgH_{2(s)}$	$\Delta H_5 =$	$-U$

total	$Mg_{(s)} + H_{2(g)} \rightarrow MgH_{2(s)}$	$\Delta H =$	ΔH_f

B Table A6 lists the first and second ionization energies for the period 3 elements [I_1(Mg) = 737.7 kJ/mol, I_2(Mg) = 1450.7 kJ/mol]. First electron affinities for all elements are given in Figure 21.5.1 [EA(H) = −72.8 kJ/mol]. Table 21.5.4 lists selected enthalpies of sublimation [ΔH_{sub}(Mg) = 147.1 kJ/mol]. Table 21.5.5 lists selected bond dissociation energies [$D(H_2)$ = 436.0 kJ/mol]. Enthalpies of formation (ΔH_f = −75.3 kJ/mol for MgH_2) are listed in Table T2. From Hess's law, ΔH_f is equal to the sum of the enthalpy changes for Reactions 1–5:

For MgH_2, U = 2701.2 kJ/mol. Once again, lattice energy provides the driving force for forming this compound because ΔH_1, ΔH_2, $\Delta H_3 > 0$. When solving this type of problem, be sure to write the chemical equation for each step and double-check that the enthalpy value used for each step has the correct sign *for the reaction in the direction it is written*.

? Exercise 21.5.3

Use data from the reference tables to calculate the lattice energy of Li_2O. Remember that the second electron affinity for oxygen [$O^-(g) + e^- \rightarrow O^{2-}(g)$] is *positive* (+744 kJ/mol).

Answer

2809 kJ/mol

Summary

Ionic compounds have strong electrostatic attractions between oppositely charged ions in a regular array. The lattice energy (U) of an ionic substance is defined as the energy required to dissociate the solid into gaseous ions; U can be calculated from the charges on the ions, the arrangement of the ions in the solid, and the internuclear distance. Because U depends on the product of the ionic charges, substances with di- or tripositive cations and/or di- or trinegative anions tend to have higher lattice energies than their singly charged counterparts. Higher lattice energies typically result in higher **melting points** and increased **hardness** because more thermal energy is needed to overcome the forces that hold the ions together. Lattice energies cannot be measured directly but are obtained from a thermochemical cycle called the **Born–Haber cycle**, in which Hess's law is used to calculate the lattice energy from the measured enthalpy of formation of the ionic compound, along with other thermochemical data. The Born–Haber cycle can be used to predict which ionic compounds are likely to form. **Sublimation**, the conversion of a solid directly to a gas, has an accompanying enthalpy change called the **enthalpy of sublimation**.

Key Takeaway

- The lattice energy is usually the most important energy factor in determining the stability of an ionic compound.

21.E: Structure and Bonding in Solids (Exercises)

21.1: Crystal Symmetry and the Unit Cell

21.2: Crystal Structure

21.3: Cohesion in Solids

21.4: Defects and Amorphous Solids

21.5: A Deeper Look: Lattice Energies of Crystals

Conceptual Problems

1. If a great deal of energy is required to form gaseous ions, why do ionic compounds form at all?
2. What are the general physical characteristics of ionic compounds?
3. Ionic compounds consist of crystalline lattices rather than discrete ion pairs. Why?
4. What factors affect the magnitude of the lattice energy of an ionic compound? What is the relationship between ionic size and lattice energy?
5. Which would have the larger lattice energy—an ionic compound consisting of a large cation and a large anion or one consisting of a large anion and a small cation? Explain your answer and any assumptions you made.
6. How would the lattice energy of an ionic compound consisting of a monovalent cation and a divalent anion compare with the lattice energy of an ionic compound containing a monovalent cation and a monovalent anion, if the internuclear distance was the same in both compounds? Explain your answer.
7. Which would have the larger lattice energy—$CrCl_2$ or $CrCl_3$—assuming similar arrangements of ions in the lattice? Explain your answer.
8. Which cation in each pair would be expected to form a chloride salt with the larger lattice energy, assuming similar arrangements of ions in the lattice? Explain your reasoning.
   1. Na^+, Mg^{2+}
   2. Li^+, Cs^+
   3. Cu^+, Cu^{2+}
9. Which cation in each pair would be expected to form an oxide with the higher melting point, assuming similar arrangements of ions in the lattice? Explain your reasoning.
   1. Mg^{2+}, Sr^{2+}
   2. Cs^+, Ba^{2+}
   3. Fe^{2+}, Fe^{3+}
10. How can a thermochemical cycle be used to determine lattice energies? Which steps in such a cycle require an input of energy?
11. Although NaOH and CH_3OH have similar formulas and molecular masses, the compounds have radically different properties. One has a high melting point, and the other is a liquid at room temperature. Which compound is which and why?

Numerical Problems

1. Arrange SrO, PbS, and PrI_3 in order of decreasing lattice energy.
2. Compare BaO and MgO with respect to each of the following properties.
   1. enthalpy of sublimation
   2. ionization energy of the metal
   3. lattice energy
   4. enthalpy of formation

3. Use a thermochemical cycle and data from Figure 7.13, Table 7.5, Table 8.2, Table 8.3 to calculate the lattice energy (U) of magnesium chloride ($MgCl_2$).
4. Would you expect the formation of SrO from its component elements to be exothermic or endothermic? Why or why not? How does the valence electron configuration of the component elements help you determine this?
5. Using the information in Problem 4 and Problem 5, predict whether CaO or $MgCl_2$ will have the higher melting point.
6. Use a thermochemical cycle and data from Table 8.2, Table 8.3, and Chapter 25 to calculate the lattice energy of calcium oxide. The first and second ionization energies of calcium are 589.8 kJ/mol and 1145.4 kJ/mol.

Answers

1. Lattice energy is directly proportional to the product of the ionic charges and inversely proportional to the internuclear distance. Therefore, PrI_3 > SrO > PbS.
2.
3. U = 2522.2 kJ/mol
4.
5. Despite the fact that Mg^{2+} is smaller than Ca^{2+}, the higher charge of O^{2-} versus Cl^{-} gives CaO a larger lattice energy than $MgCl_2$. Consequently, we expect CaO to have the higher melting point.

CHAPTER OVERVIEW

22: Inorganic Materials

An General Chemistry Libretexts Textmap organized around the textbook
Principles of Modern Chemistry
by Oxtoby, Gillis, and Campion

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI
XVII XVIII XIX XX XXI XXII XXIII • **Homework Exercises**

Template:HideTOC

Topic hierarchy

22.1: Minerals: Naturally Occurring Inorganic Minerals

22.2: Properties of Ceramics

22.3: Silicate Ceramics

22.4: Nonsilicate Ceramics

22.5: Electrical Conduction in Materials

22.6: Band Theory of Conduction

22.7: Semiconductors

22.8: Pigments and Phosphors: Optical Displays

CHAPTER OVERVIEW

23: Polymeric Materials and Soft Condensed Matter

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

I II III IV V VI VII VIII IX X XI XII XIII XIV XV XVI
XVII XVIII XIX XX XXI XXII XXIII ● **Homework Exercises**

Template:HideTOC

A polymer is a large molecule, or macromolecule, composed of many repeated subunits. Because of their broad range of properties, both synthetic and natural polymers play essential and ubiquitous roles in everyday life. Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function.

23.1: Polymerization Reactions for Synthetic Polymers

Prior to the early 1920's, chemists doubted the existence of molecules having molecular weights greater than a few thousand. This limiting view was challenged by Hermann Staudinger, a German chemist with experience in studying natural compounds such as rubber and cellulose. In contrast to the prevailing rationalization of these substances as aggregates of small molecules, Staudinger proposed they were made up of **macromolecules** composed of 10,000 or more atoms. He formulated a **polymeric** structure for rubber, based on a repeating isoprene unit (referred to as a monomer). For his contributions to chemistry, Staudinger received the 1953 Nobel Prize. The terms **polymer** and **monomer** were derived from the Greek roots poly (many), mono (one) and meros (part).

Recognition that polymeric macromolecules make up many important natural materials was followed by the creation of synthetic analogs having a variety of properties. Indeed, applications of these materials as fibers, flexible films, adhesives, resistant paints and tough but light solids have transformed modern society. Some important examples of these substances are discussed in the following sections.

Contributors and Attributions

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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23.2: Applications for Synthetic Polymers

23.3: Liquid Crystals

11.08: Liquid Crystals

SECTION OVERVIEW

23.4: Natural Polymers

Polymers are long chain, giant organic molecules are assembled from many smaller molecules called monomers. Polymers consist of many repeating monomer units in long chains, sometimes with *branching* or *cross-linking* between the chains.

Template:HideTOC

Index

Glossary

absolute zero (0 K) | The lowest possible temperature that can be theoretically achieved; it corresponds to −273.15°C.

absorption spectrum | A spectrum produced by the absorption of light by ground-state atoms.

acid ionization constant (K_a) | An equilibrium constant for the ionization (dissociation) of a weak acid (HA) with water, + ⇌ + in which the concentration of water is treated as a constant: =

acid rain | Precipitation that is dramatically more acidic because of human activities.

acid–base indicator | A compound added in small amounts to an acid–base titration to signal the equivalence point by changing color.

actinides | Any of the 14 elements between (thorium) and (lawrencium).

activation energy (E_a) | The energy barrier or threshold that corresponds to the minimum amount of energy the particles in a reaction must have to react when they colllide.

activity (*A*) | The decrease in the number of a radioisotope's nuclei per unit time:

adduct | The product of a reaction between a Lewis acid and a Lewis base with a coordinate covalent bond.

aerosols | A dispersion of solid or liquid particles in a gas.

alcohol | A class of organic compounds obtained by replacing one or more of the hydrogen atoms of a hydrocarbon with an −OH group.

aliphatic hydrocarbons | Alkanes, alkenes, alkynes, and cyclic hydrocarbons (hydrocarbons that are not aromatic).

amalgams | A solution (usually a solid solution) of a metal in liquid mercury.

amine | An organic compound that has the general formula , where R is an alkyl group. Amines, like ammonia, are bases.

amorphous solid | A solid with no particular structural order.

amphiprotic | Substances that can behave as either an acid or a base in a chemical reaction, depending on the nature of the other reactant(s).

amphoteric | When substances can behave as both an acid and a base.

amplification mechanism | A process by which elements that are present in trace amounts can exert large effects on the health of an organism.

anions | An ion that has fewer protons than electrons, resulting in a net negative charge.

anisotropic | An arrangement of molecules in which their properties depend on the direction they are measured.

antibonding molecular orbital | A molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructuve reinforcement of the wave functions.

aqueous solution | A solution in which water is the solvent.

aromatic hydrocarbons | An unsaturated hydrocarbon consisting of a ring of six carbon atoms with alternating single and double bonds.

Arrhenius equation | An expression that summarizes the collision model of chemical kinetics:

atmosphere (atm) | Also referred to as standard atmospheric pressure, it is the atmospheric pressure required to support a column of mercury exactly 760 mm tall.

atmosphere (atm) | Also referred to as standard atmospheric pressure, it is the atmospheric pressure required to support a column of mercury exactly 760 mm tall.

atomic mass unit (amu) | One-twelfth of the mass of one atom of ; .

atomic mass unit (amu) | One-twelfth of the mass of one atom of ; .

atomic orbital | A wave function with an allowed combination of , , and quantum numbers.

atomic orbital | A wave function with an allowed combination of , , and quantum numbers.

atoms | The fundamental, individual particles of which matter is composed.

atoms | The fundamental, individual particles of which matter is composed.

aufbau principle | The process used to build up the periodic table by adding protons one by one to the nucleus and adding the corresponding electrons to the lowest-energy orbital available without violating the Pauli exclusion principle.

aufbau principle | The process used to build up the periodic table by adding protons one by one to the nucleus and adding the corresponding electrons to the lowest-energy orbital available without violating the Pauli exclusion principle.

average reaction rate | The reaction rate calculated for a given time interval from the concentrations of either the reactant or one of the products at the beginning of the interval time and at the end of the interval

average reaction rate | The reaction rate calculated for a given time interval from the concentrations of either the reactant or one of the products at the beginning of the interval time and at the end of the interval

Avogadro's law | A law that states that at constant temperature and pressure, the volume of a sample of gas is directly proportional to the number of moles of gas in the sample.

Avogadro's law | A law that states that at constant temperature and pressure, the volume of a sample of gas is directly proportional to the number of moles of gas in the sample.

Avogadro's number | The number of units (e.g., atoms, molecules, or formula units) in 1 mol: .

Avogadro's number | The number of units (e.g., atoms, molecules, or formula units) in 1 mol: .

azimuthal quantum number (l) | One of three quantum numbers that discribes the shape of the region of space occupied by an electron.

azimuthal quantum number (l) | One of three quantum numbers that discribes the shape of the region of space occupied by an electron.

band gap | The difference in energy between the highest level of one energy band and the lowest level of the band above it, which represents a set of forbidden energies that do not correspond to any allowed combinations of atomic orbitals.

band gap | The difference in energy between the highest level of one energy band and the lowest level of the band above it, which represents a set of forbidden energies that do not correspond to any allowed combinations of atomic orbitals.

band theory | A theory used to describe the bonding in metals and semiconductors.

band theory | A theory used to describe the bonding in metals and semiconductors.

bandwidth | The difference in energy between the highest and lowest energy levels in an energy band.

bandwidth | The difference in energy between the highest and lowest energy levels in an energy band.

barometer | A device used to measure atmospheric pressure.

barometer | A device used to measure atmospheric pressure.

base | A substance that produces one or more hydroxide ions and a cation when dissolved in aqueous solution, thereby forming a basic solution.

base | A substance that produces one or more hydroxide ions and a cation when dissolved in aqueous solution, thereby forming a basic solution.

base ionization constant | An equilibrium constant for the reaction of a weak base (B) with water, in which the concentration of water is treated as a constant. Abbreviation: K_b

base ionization constant (K_b) | An equilibrium constant for the reaction of a weak base (B) with water, + ⇌ + in which the concentration of water is treated as a constant:
=

bases | A substance that produces one or more hydroxide ions and a cation when dissolved in aqueous solution, thereby forming a basic solution.

bases | A substance that produces one or more hydroxide ions and a cation when dissolved in aqueous solution, thereby forming a basic solution.

bilayers | A two-dimensional sheet consisting of a double layer of phospholipid molecules arranged tail to tail.

bilayers | A two-dimensional sheet consisting of a double layer of phospholipid molecules arranged tail to tail.

binary ionic compound | An ionic compound that contains only two elements, one present as a cation and one as an anion.

binary ionic compound | An ionic compound that contains only two elements, one present as a cation and one as an anion.

biochemistry | The application of chemistry to the study of biological processes.

biochemistry | The application of chemistry to the study of biological processes.

blackbody radiation | Electromagnetic radiation whose wavelength and color depends on the temperature of the object.

blackbody radiation | Electromagnetic radiation whose wavelength and color depends on the temperature of the object.

boiling point elevation (ΔT_b) | The difference between the boiling point of a solution and the boiling point of the pure solvent.

boiling point elevation (ΔT_b) | The difference between the boiling point of a solution and the boiling point of the pure solvent.

Boltzmann distributions | A curve that shows the distribution of molecular speeds at a given temperature.

Boltzmann distributions | A curve that shows the distribution of molecular speeds at a given temperature.

bomb calorimeter | A device used to measure energy changes in chemical processes.

bomb calorimeter | A device used to measure energy changes in chemical processes.

bond distance(r_0) | The optimal internuclear distance between two bonded atoms.

bond distance(r_0) | The optimal internuclear distance between two bonded atoms.

bond energy | The enthalpy change that occurs when a given bond in a gaseous molecule is broken.

bond energy | The enthalpy change that occurs when a given bond in a gaseous molecule is broken.

bond order | The number of electron pairs that hold two atoms together.

bond order | The number of electron pairs that hold two atoms together.

bond order | One-half the net number of bonding electrons in a molecule.

bond order | One-half the net number of bonding electrons in a molecule.

Born–Haber cycle | A thermochemical cycle that decribes the process in which an ionic solid is conceptually formed from its component elements in a stepwise manner.

Born–Haber cycle | A thermochemical cycle that decribes the process in which an ionic solid is conceptually formed from its component elements in a stepwise manner.

Boyle’s law | A law that states that at constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure.

Boyle’s law | A law that states that at constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure.

Bragg equation | The equation that describes the relationship between two x-ray beams diffracted from different planes of atoms:

Bragg equation | The equation that describes the relationship between two x-ray beams diffracted from different planes of atoms:

buffer capacity | The amount of strong acid or strong base that a buffer solution can absorb before the pH changes dramatically.

Buffers | Solutions that maintain a relatively constant pH when an acid or a base is added.

Calorie | A unit used to indicate the caloric content of food. It is equal to 1 kilocalorie (1 kcal).

Calorie | A unit used to indicate the caloric content of food. It is equal to 1 kilocalorie (1 kcal).

calories (cal) | A non-SI unit of energy: 1 cal = 4.184 J exactly.

calories (cal) | A non-SI unit of energy: 1 cal = 4.184 J exactly.

Calorimetry | A set of techniques used to measure enthalpy changes in chemical processes.

Calorimetry | A set of techniques used to measure enthalpy changes in chemical processes.

capillary action | The tendency of a polar liquid to rise against gravity into a small-diameter glass tube.

capillary action | The tendency of a polar liquid to rise against gravity into a small-diameter glass tube.

carbon cycle | The distribution and flow of carbon throughout the planet.

carbon cycle | The distribution and flow of carbon throughout the planet.

carboxylic acids | An organic compound that contains an −OH group covalently bonded to the carbon atom of a carbonyl group. The general formula of a carboxylic acid is . In water a carboxylic acid dissociates to produce an acidic solution.

carboxylic acids | An organic compound that contains an −OH group covalently bonded to the carbon atom of a carbonyl group. The general formula of a carboxylic acid is . In water a carboxylic acid dissociates to produce an acidic solution.

catalysis | The acceleration of a chemical reaction by a catalyst.

catalysis | The acceleration of a chemical reaction by a catalyst.

catalysts | A substance that participates in a reaction and causes it to occur more rapidly but that can be recovered unchanged at the end of the reaction and reused. Catalysts may also control which products are formed in a reaction.

catalysts | A substance that participates in a reaction and causes it to occur more rapidly but that can be recovered unchanged at the end of the reaction and reused. Catalysts may also control which products are formed in a reaction.

cell | A collection of molecules, capable of reproducing itself, that is surrounded by a phospholipid bilayer.

cell | A collection of molecules, capable of reproducing itself, that is surrounded by a phospholipid bilayer.

ceramic | Any nonmetallic inorganic solid that is strong eneough to be used in structural applications.

ceramic | Any nonmetallic inorganic solid that is strong eneough to be used in structural applications.

Ceramic-matrix composites | A composite consisting of reinforcing fibers embedded in a ceramic matrix.

Ceramic-matrix composites | A composite consisting of reinforcing fibers embedded in a ceramic matrix.

cesium chloride structure | The unit cell for many ionic compounds with relatively large cations and a 1:1 cation:anion ratio.

cesium chloride structure | The unit cell for many ionic compounds with relatively large cations and a 1:1 cation:anion ratio.

chain reactions | A reaction mechanism in which one or more elementary reactions that contain a highly reactive species repeat again and again during the reaction process.

chain reactions | A reaction mechanism in which one or more elementary reactions that contain a highly reactive species repeat again and again during the reaction process.

chalcogens | The elements in group 16 of the periodic table.

chalcogens | The elements in group 16 of the periodic table.

change in enthalpy (ΔH) | At constant pressure, the amount of heat transferred from the surroundings to the system or vice versa: .

change in enthalpy (ΔH) | At constant pressure, the amount of heat transferred from the surroundings to the system or vice versa: .

Charles’s law | A law that states that at constant pressure, the volume of a fixed amount of gas is directly proportional to its absolute temperature (in kelvins).

Charles’s law | A law that states that at constant pressure, the volume of a fixed amount of gas is directly proportional to its absolute temperature (in kelvins).

chemical bonds | An attractive interaction between atoms that holds them together in compounds.

chemical bonds | An attractive interaction between atoms that holds them together in compounds.

chemical change | A process in which the chemical composition of one or more substances is altered.

chemical change | A process in which the chemical composition of one or more substances is altered.

chemical energy | One of the five forms of energy, chemical energy is stored within a chemical compound because of a particular arrangement of atoms. The other four forms of energy are radiant, thermal, nuclear, and electrical.

chemical energy | One of the five forms of energy, chemical energy is stored within a chemical compound because of a particular arrangement of atoms. The other four forms of energy are radiant, thermal, nuclear, and electrical.

chemical equilibrium | The point at which the forward and reverse reaction rates become the same so that the net composition of the system no longer changes with time.

Chemical properties | The characteristic ability of a substance to react to form new substances.

Chemical properties | The characteristic ability of a substance to react to form new substances.

chemical reactions | A process in which a substance is converted to one or more other substances with different compositions and properties.

Chemistry | The study of matter and the changes that material substances undergo.

Chemistry | The study of matter and the changes that material substances undergo.

cholesteric phase | One of three different ways that most liquid crystals can orient themselves. The molecules are arranged in planes (similar to the smectic phase), but each layer is rotated by a certain amount with respect to those above and below it, giving it a helical structure.

cholesteric phase | One of three different ways that most liquid crystals can orient themselves. The molecules are arranged in planes (similar to the smectic phase), but each layer is rotated by a certain amount with respect to those above and below it, giving it a helical structure.

Clausius–Clapeyron equation | A linear relationship that expresses the nonlinear relationship between the vapor pressure of a liquid and temperature: ln where is pressure, is the heat of vaporization, is the universal gas constant, is the absolute temperature, and C is a constant. The Clausius–Clapeyron equation can be used to calculate the heat of vaporization of a liquid from its measured vapor pressure at two or more temperatures.

Clausius–Clapeyron equation | A linear relationship that expresses the nonlinear relationship between the vapor pressure of a liquid and temperature: ln where is pressure, is the heat of vaporization, is the universal gas constant, is the absolute temperature, and C is a constant. The Clausius–Clapeyron equation can be used to calculate the heat of vaporization of a liquid from its measured vapor pressure at two or more temperatures.

Coal | A complex solid material derived primarily from plants that died and were buried hundreds of millions of years ago and were subsequently subjected to high temperatures and pressures. It is used as a fuel.

Coal | A complex solid material derived primarily from plants that died and were buried hundreds of millions of years ago and were subsequently subjected to high temperatures and pressures. It is used as a fuel.

coefficient | A number greater than 1 preceding a formula in a balanced chemical equation and indicating the number of atoms, molecules, or formula units of a reactant or a product.

coefficient | A number greater than 1 preceding a formula in a balanced chemical equation and indicating the number of atoms, molecules, or formula units of a reactant or a product.

colligative properties | A property of a solution that depends primarily on the *number* of solute particles rather than the *kind* of solute particles.

colligative properties | A property of a solution that depends primarily on the *number* of solute particles rather than the *kind* of solute particles.

colloid | A heterogeneous mixture of particles with diameters of about 2–500 nm that are distributed throughout a second phase and do not separate from the dispersing phase on standing.

colloid | A heterogeneous mixture of particles with diameters of about 2–500 nm that are distributed throughout a second phase and do not separate from the dispersing phase on standing.

combustion | The burning of a material in an oxygen atmosphere.

combustion | The burning of a material in an oxygen atmosphere.

combustion reaction | An oxidation–reduction reaction in which the oxidant is .

combustion reaction | An oxidation–reduction reaction in which the oxidant is .

common ion effect | The shift in equilibrium that results when a strong electrolyte containing one ion in common with a reaction system that is at equilibrium is added to the system.

complete ionic equation | A chemical equation that shows which ions and molecules are hydrated and which are present in other forms and phases.

complete ionic equation | A chemical equation that shows which ions and molecules are hydrated and which are present in other forms and phases.

Composite materials | A material that consists of at least two distinct phases: the matrix (which constitutes the bulk of the material) and fibers or granules that are embedded within the matrix.

Composite materials | A material that consists of at least two distinct phases: the matrix (which constitutes the bulk of the material) and fibers or granules that are embedded within the matrix.

concentration | The quantity of solute that is dissolved in a particular quantity of solvent or solution.

concentration | The quantity of solute that is dissolved in a particular quantity of solvent or solution.

concentration | The quantity of solute that is dissolved in a particular quantity of solvent or solution.

concentration | The quantity of solute that is dissolved in a particular quantity of solvent or solution.

condensation | The physical process by which atoms or molecules in the vapor phase enter the liquid phase.

condensation | The physical process by which atoms or molecules in the vapor phase enter the liquid phase.

conduction band | The band of empty molecular orbitals in a semiconductor.

conduction band | The band of empty molecular orbitals in a semiconductor.

conjugate acid–base pair | An acid and a base that differ by only one hydrogen ion.

conjugate acid–base pair | An acid and a base that differ by only one hydrogen ion.

conjugate acid–base pairs | An acid and a base that differ by only one hydrogen ion. All acid–base reactions involve two conjugate acid–base pairs, the Brønsted–Lowry acid and the base it forms after donating its proton, and the Brønsted–Lowry base and the acid it forms after accepting a proton.

conjugate acid–base pairs | An acid and a base that differ by only one hydrogen ion. All acid–base reactions involve two conjugate acid–base pairs, the Brønsted–Lowry acid and the base it forms after donating its proton, and the Brønsted–Lowry base and the acid it forms after accepting a proton.

constant-pressure calorimeter | A device used to measure enthalpy changes in chemical processes at constant pressure.

constant-pressure calorimeter | A device used to measure enthalpy changes in chemical processes at constant pressure.

Cooper pairs | Pairs of electrons that migrate through a superconducting material as a unit.

Cooper pairs | Pairs of electrons that migrate through a superconducting material as a unit.

coordinate covalent bond | A covalent bond in which both electrons come from the same atom.

coordinate covalent bond | A covalent bond in which both electrons come from the same atom.

coordination number | The number of nearest neighbors in a solid structure.

coordination number | The number of nearest neighbors in a solid structure.

covalent atomic radius (r_{cov}) | Half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule.

covalent atomic radius (r_{cov}) | Half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule.

covalent bond | The electrostatic attraction between the positively charged nuclei of the bonded atoms and the negatively charged electrons they share.

covalent bond | The electrostatic attraction between the positively charged nuclei of the bonded atoms and the negatively charged electrons they share.

Covalent solids | A solid that consists of two- or three-dimensional networks of atoms held together by covalent bonds.

Covalent solids | A solid that consists of two- or three-dimensional networks of atoms held together by covalent bonds.

critical point | The combination of the critical temperature and the critical pressure of a substance.

critical point | The combination of the critical temperature and the critical pressure of a substance.

crown ethers | Cyclic polyether with four or more oxygen atoms separated by two or three carbon atoms. All crown ethers have a central cavity that can accommodate a metal ion coordinated to the ring of oxygen atoms.

crown ethers | Cyclic polyether with four or more oxygen atoms separated by two or three carbon atoms. All crown ethers have a central cavity that can accommodate a metal ion coordinated to the ring of oxygen atoms.

cryogenic liquids | An ultracold liquid formed from the liquefaction of gases.

cryogenic liquids | An ultracold liquid formed from the liquefaction of gases.

Cryptands | Consisting of three chains connected by two nitrogen atoms, cryptands have a central cavity that can encapsulate a metal ion coordinated to the oxygen and nitrogen atoms.

Cryptands | Consisting of three chains connected by two nitrogen atoms, cryptands have a central cavity that can encapsulate a metal ion coordinated to the oxygen and nitrogen atoms.

Crystallization | A physical process used to separate homogeneous mixtures (solutions) into their component substances. Crystallization separates mixtures based on differences in their solubilities.

Crystallization | A physical process used to separate homogeneous mixtures (solutions) into their component substances. Crystallization separates mixtures based on differences in their solubilities.

cubic close-packed (ccp) structure | One of two variants of the close-packed arrangement—the most efficient way to pack spheres in a lattice—in which the atomic positions alter from layer to layer in an ABCABC… pattern.

cubic close-packed (ccp) structure | One of two variants of the close-packed arrangement—the most efficient way to pack spheres in a lattice—in which the atomic positions alter from layer to layer in an ABCABC… pattern.

cyclic hydrocarbon | A hydrocarbon in which the ends of the carbon chain are connected to form a ring of covalently bonded carbon atoms.

cyclic hydrocarbon | A hydrocarbon in which the ends of the carbon chain are connected to form a ring of covalently bonded carbon atoms.

Dalton's law of partial pressures | A law that states that the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases.

Dalton's law of partial pressures | A law that states that the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases.

defects | Errors in an idealized crystal lattice.

defects | Errors in an idealized crystal lattice.

Deformation | A distortion that occurs when a dislocation moves through a crystal.

Deformation | A distortion that occurs when a dislocation moves through a crystal.

degenerate | Having the same energy.

degenerate | Having the same energy.

density (d) | An intensive property of matter, density is the mass per unit volume (usually expressed in g/cm^3). At a given temperature, the density of a substance is a constant.

density (d) | An intensive property of matter, density is the mass per unit volume (usually expressed in g/cm^3). At a given temperature, the density of a substance is a constant.

dialysis | A process that uses a semipermeable membrane with pores large enough to allow small solute molecules and solvent molecules to pass through but not large solute molecules.

dialysis | A process that uses a semipermeable membrane with pores large enough to allow small solute molecules and solvent molecules to pass through but not large solute molecules.

dielectric constant (ε) | A constant that expresses the ability of a bulk substance to decrease the electrostatic forces between two charged particles.

dielectric constant (ε) | A constant that expresses the ability of a bulk substance to decrease the electrostatic forces between two charged particles.

dipole moment | The product of the partial charge on the bonded atoms and the distance between the partial charges: , where is measured in coulombs (C) and in meters (m).

dipole moment | The product of the partial charge on the bonded atoms and the distance between the partial charges: , where is measured in coulombs (C) and in meters (m).

dipole–dipole interactions | A kind of intermolecular interaction (force) that results between molecules with net dipole moments.

dipole–dipole interactions | A kind of intermolecular interaction (force) that results between molecules with net dipole moments.

Distillation | A physical process used to separate homogeneous mixtures (solutions) into their component substances. Distillation makes use of differences in the volatilities of the component substances.

Distillation | A physical process used to separate homogeneous mixtures (solutions) into their component substances. Distillation makes use of differences in the volatilities of the component substances.

edge dislocation | A crystal defect that results from the insertion of an extra plane of atoms into part of the crystal lattice.

edge dislocation | A crystal defect that results from the insertion of an extra plane of atoms into part of the crystal lattice.

effusion | The escape of a gas through a small (usually microscopic) opening into an evacuated space.

effusion | The escape of a gas through a small (usually microscopic) opening into an evacuated space.

electrical insulators | A material that conducts electricity poorly because its valence bands are full.

electrical insulators | A material that conducts electricity poorly because its valence bands are full.

electron affinity(EA) | The energy change that occurs when an electron is added to a gaseous atom:

electron affinity(EA) | The energy change that occurs when an electron is added to a gaseous atom:

electron configuration | The arrangement of an element's electrons in its atomic orbitals.

electron configuration | The arrangement of an element's electrons in its atomic orbitals.

electron density | Electron distributions that are represented as standing waves.

electron density | Electron distributions that are represented as standing waves.

electron sea | Valence electrons that are delocalized throughout a metallic solid.

electron sea | Valence electrons that are delocalized throughout a metallic solid.

electron shielding | The effect by which electrons closer to the nucleus neutralize a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between the nucleus and an electron father away.

electron shielding | The effect by which electrons closer to the nucleus neutralize a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between the nucleus and an electron father away.

electron spin | The magnetic moment that results when an electron spins. Electrons have two possible orientations (spin up and spin down), which are described by a fourth quantum number (m_s).

electron spin | The magnetic moment that results when an electron spins. Electrons have two possible orientations (spin up and spin down), which are described by a fourth quantum number (m_s).

Electron-deficient molecules | A compound that has less than an octet of electrons around one atom.

Electron-deficient molecules | A compound that has less than an octet of electrons around one atom.

electronegativity | The relative ability of an atom to attract electrons to itself in a chemical compound.

electronegativity | The relative ability of an atom to attract electrons to itself in a chemical compound.

elementary reaction | Each of the complex series of reactions that take place in a stepwise fashion to convert reactants to products.

elementary reaction | Each of the complex series of reactions that take place in a stepwise fashion to convert reactants to products.

Emulsions | A dispersion of one liquid phase in another liquid with which it is immiscible.

Emulsions | A dispersion of one liquid phase in another liquid with which it is immiscible.

endothermic | A process in which heat is transferred *to* a system *from* its surroundings.

endothermic | A process in which heat is transferred *to* a system *from* its surroundings.

endpoint | The point in a titration at which an indicator changes color.

endpoint | The point in a titration at which an indicator changes color.

energy-level diagram | A schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals.

energy-level diagram | A schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals.

enthalpy (H) | The sum of a system's internal energy and the product of its pressure and volume :

enthalpy (H) | The sum of a system's internal energy and the product of its pressure and volume :

Enthalpy of formation (ΔH_f) | The enthalpy change for the formation of 1 mol of a compound from its component elements.

Enthalpy of formation (ΔH_f) | The enthalpy change for the formation of 1 mol of a compound from its component elements.

enthalpy of reaction (ΔH_{rxn}) | The change in enthalpy that occurs during a chemical reaction.

enthalpy of reaction (ΔH_{rxn}) | The change in enthalpy that occurs during a chemical reaction.

enthalpy of sublimation (ΔH_{sub}) | The enthalpy change that accompanies the conversion of a solid directly to a gas.

enthalpy of sublimation (ΔH_{sub}) | The enthalpy change that accompanies the conversion of a solid directly to a gas.

enthalpy of sublimation(ΔH_{sub}) | The enthalpy change that accompanies the conversion of a solid directly to a gas.

enthalpy of sublimation(ΔH_{sub}) | The enthalpy change that accompanies the conversion of a solid directly to a gas.

entropy(S) | The degree of disorder in a thermodynamic system. The greater the number of possible microstates for a system, the higher the entropy.

entropy(S) | The degree of disorder in a thermodynamic system. The greater the number of possible microstates for a system, the higher the entropy.

enzyme | A catalyst that occurs naturally in living organisms and catalyzes biological reactions.

enzyme | A catalyst that occurs naturally in living organisms and catalyzes biological reactions.

Enzyme inhibitors | Substances that decrease the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of the enzyme, thus slowing or preventing a reaction from occurring.

Enzyme inhibitors | Substances that decrease the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of the enzyme, thus slowing or preventing a reaction from occurring.

enzymes | Catalysts that occur naturally in living organisms and that catalyze biological reactions.

enzymes | Catalysts that occur naturally in living organisms and that catalyze biological reactions.

equilibrium | The point at which the rates of the forward and reverse reactions become the same, so that the net composition of the system no longer changes with time.

equilibrium | The point at which the rates of the forward and reverse reactions become the same, so that the net composition of the system no longer changes with time.

equilibrium constant (K) | The ratio of the rate constants for the forward reaction and the reverse reaction; that is, It is also the equilibrium constant calculated from solution concentrations: for the general reaction in which each component is in solution.

equilibrium constant (K) | The ratio of the rate constants for the forward reaction and the reverse reaction; that is, It is also the equilibrium constant calculated from solution concentrations: for the general reaction in which each component is in solution.

equilibrium constant expression | For a balanced chemical equation, the ratio is for the general reaction

equilibrium constant expression | For a balanced chemical equation, the ratio is for the general reaction

equilibrium vapor pressure | The pressure exerted by a vapor in dynamic equilibrium with its liquid.

equilibrium vapor pressure | The pressure exerted by a vapor in dynamic equilibrium with its liquid.

equivalence point | The point in a titration where a stoichiometric amount (i.e., the amount required to react completely with the unknown) of the titrant has been added.

equivalence point | The point in a titration where a stoichiometric amount (i.e., the amount required to react completely with the unknown) of the titrant has been added.

equivalence point | The point in a titration where a stoichiometric amount of the titrant has been added.

essential elements | Any of the 19 elements that are absolutely required in the human diet for survival. An additional seven elements are thought to be essential for humans.

essential elements | Any of the 19 elements that are absolutely required in the human diet for survival. An additional seven elements are thought to be essential for humans.

Essential trace elements | Elements that are required for the growth of most organisms.

Essential trace elements | Elements that are required for the growth of most organisms.

evaporation (or vaporization) | The physical process by which atoms or molecules in the liquid phase enter the gas or vapor phase.

evaporation (or vaporization) | The physical process by which atoms or molecules in the liquid phase enter the gas or vapor phase.

exact numbers | An integer obtained either by counting objects or from definitions (e.g., 1 in. = 2.54 cm). Exact numbers have infinitely many significant figures.

exact numbers | An integer obtained either by counting objects or from definitions (e.g., 1 in. = 2.54 cm). Exact numbers have infinitely many significant figures.

excited state | Any arrangement of electrons that is higher in energy than the ground state.

excited state | Any arrangement of electrons that is higher in energy than the ground state.

exothermic | A process in which heat is transferred *from* a system *to* its surroundings.

exothermic | A process in which heat is transferred *from* a system *to* its surroundings.

expanded-valence molecules | A compound with more than an octet of electrons around an atom.

expanded-valence molecules | A compound with more than an octet of electrons around an atom.

***f* block** | The elements in the periodic table in which the $(n-2)f$ orbitals are being filled.

***f* block** | The elements in the periodic table in which the $(n-2)f$ orbitals are being filled.

face-centered cubic (fcc) | A cubic unit cell with eight component atoms, molecules, or ions located at the corners of a cube plus an identical component in the center of each face of the cube.

face-centered cubic (fcc) | A cubic unit cell with eight component atoms, molecules, or ions located at the corners of a cube plus an identical component in the center of each face of the cube.

fibers | A particle of a synthetic polymer that is more than 100 times longer than it is wide.

fibers | A particle of a synthetic polymer that is more than 100 times longer than it is wide.

first-order reaction | A reaction whose rate is directly proportional to the concentration of one reactant.

first-order reaction | A reaction whose rate is directly proportional to the concentration of one reactant.

formal charge | The difference between the number of valence electrons in a free atom and the number of electrons assigned to it in a particular Lewis electron structure.

formal charge | The difference between the number of valence electrons in a free atom and the number of electrons assigned to it in a particular Lewis electron structure.

formula mass | The sum of the atomic masses of all the elements in the empirical formula, each multiplied by its subscript.

formula mass | The sum of the atomic masses of all the elements in the empirical formula, each multiplied by its subscript.

formula unit | The absolute grouping of atoms or ions represented by the empirical formula.

formula unit | The absolute grouping of atoms or ions represented by the empirical formula.

fractional crystallization | The separation of compounds based on their relative solubilities in a given solvent.

fractional crystallization | The separation of compounds based on their relative solubilities in a given solvent.

freezing point depression (ΔT_f) | The difference between the freezing point of a pure solvent and the freezing point of the solution.

freezing point depression (ΔT_f) | The difference between the freezing point of a pure solvent and the freezing point of the solution.

Frenkel defect | A defect in an ionic lattice that occurs when one of the ions is in the wrong position.

Frenkel defect | A defect in an ionic lattice that occurs when one of the ions is in the wrong position.

frequency factor | A constant in the Arrhenius equation, it converts concentrations to collisions per second.

frequency factor | A constant in the Arrhenius equation, it converts concentrations to collisions per second.

fundamental | The lowest-energy standing wave.

fundamental | The lowest-energy standing wave.

fusion (or melting) | The conversion of a solid to a liquid.

fusion (or melting) | The conversion of a solid to a liquid.

gas constant | A proportionality constant that is used in the ideal gas law.

gas constant | A proportionality constant that is used in the ideal gas law.

glass | An amorphous, translucent solid. A glass is a solid that has been cooled too quickly to form ordered crystals.

glass | An amorphous, translucent solid. A glass is a solid that has been cooled too quickly to form ordered crystals.

Graham's law | A law that states that the rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass.

Graham's law | A law that states that the rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass.

grain boundary | The place where two grains in a solid intersect.

grain boundary | The place where two grains in a solid intersect.

greenhouse effect | The phenomenon in which substances absorb thermal energy radiated by Earth, thus trapping thermal energy in the atmosphere.

greenhouse effect | The phenomenon in which substances absorb thermal energy radiated by Earth, thus trapping thermal energy in the atmosphere.

greenhouse gases | A substance that absorbs thermal energy radiated by Earth, thus trapping thermal energy in the atmosphere.

greenhouse gases | A substance that absorbs thermal energy radiated by Earth, thus trapping thermal energy in the atmosphere.

group-transfer reactions | A reaction in which a recognizable functional group is transferred from one molecule to another.

group-transfer reactions | A reaction in which a recognizable functional group is transferred from one molecule to another.

half-life | The period of time it takes for the concentration of a reactant to decrease to one-half its initial value.

half-life | The period of time it takes for the concentration of a reactant to decrease to one-half its initial value.

hardness | The resistance of ionic materials to scratching or abrasion.

hardness | The resistance of ionic materials to scratching or abrasion.

heat (q) | Thermal energy that can be transformed from an object at one temperature to an object at another temperature.

heat (q) | Thermal energy that can be transformed from an object at one temperature to an object at another temperature.

heat capacity (C) | The amount of energy needed to raise the temperature of an object 1°C. The units of heat capacity are joules per degree Celsius

heat capacity (C) | The amount of energy needed to raise the temperature of an object 1°C. The units of heat capacity are joules per degree Celsius

Heisenberg uncertainty principle | A principle stating that the uncertainty in the position of a particle multiplied by the uncertainty in its momentum is greater than or equal to Planck's constant divided by 4π:

Heisenberg uncertainty principle | A principle stating that the uncertainty in the position of a particle multiplied by the uncertainty in its momentum is greater than or equal to Planck's constant divided by 4π:

Henderson-Hasselbalch equation | A rearranged version of the equilibrium constant expression that provides a direct way to calculate the pH of a buffer solution: pH = + log([base]/[acid]).

Henry's law | An equation that quantifies the relationship between the pressure and the solubility of a gas:

Henry's law | An equation that quantifies the relationship between the pressure and the solubility of a gas:

Hess's law | The enthalpy change for an overall reaction is the sum of the values for the individual reactions.

Hess's law | The enthalpy change for an overall reaction is the sum of the values for the individual reactions.

heterogeneous | A mixture in which a material is not completely uniform throughout.

heterogeneous | A mixture in which a material is not completely uniform throughout.

heterogeneous catalysis | A catalytic reaction in which the catalyst is in a different phase from the reactants.

heterogeneous catalysis | A catalytic reaction in which the catalyst is in a different phase from the reactants.

heterogeneous catalyst | A catalyst that is in a different physical state than the reactants.

heterogeneous catalyst | A catalyst that is in a different physical state than the reactants.

heterogeneous equilibrium | An equilibrium in which the reactants of an equilibrium reaction, the products, or both are in more than one phase.

heterogeneous equilibrium | An equilibrium in which the reactants of an equilibrium reaction, the products, or both are in more than one phase.

heteronuclear diatomic molecules | A molecule that consists of two atoms of different elements.

heteronuclear diatomic molecules | A molecule that consists of two atoms of different elements.

high-temperature superconductors | A material that becomes a superconductor at temperatures greater than 30 K.

high-temperature superconductors | A material that becomes a superconductor at temperatures greater than 30 K.

homogeneous | A mixture in which all portions of a material are in the same state, have no visible boundaries, and are uniform throughout.

homogeneous | A mixture in which all portions of a material are in the same state, have no visible boundaries, and are uniform throughout.

homogeneous catalysis | A catalytic reaction in which the catalyst is uniformly dispersed throughout the reactant mixture to form a solution.

homogeneous catalysis | A catalytic reaction in which the catalyst is uniformly dispersed throughout the reactant mixture to form a solution.

homonuclear diatomic molecule | A molecule that consists of two atoms of the same element.

homonuclear diatomic molecule | A molecule that consists of two atoms of the same element.

Hund's rule | A rule stating that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals.

Hund's rule | A rule stating that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals.

hybrid atomic orbitals | New atomic orbitals formed from the process of hybridization.

hybrid atomic orbitals | New atomic orbitals formed from the process of hybridization.

hydrated ions | Individual cations and anions that are each surrounded by their own shell of water molecules.

hydrated ions | Individual cations and anions that are each surrounded by their own shell of water molecules.

hydration | The process of surrounding solute particles with water molecules.

hydration | The process of surrounding solute particles with water molecules.

hydrogen bonds | An unusually strong dipole-dipole interaction (intermolecular force) that results when hydrogen is bonded to very electronegative elements, such as O, N, and F.

hydrogen bonds | An unusually strong dipole-dipole interaction (intermolecular force) that results when hydrogen is bonded to very electronegative elements, such as O, N, and F.

hydrolysis reactions | A chemical reaction in which a salt reacts with water to yield an acidic or a basic solution.

hydronium ion | The ion, represented as

hydronium ion | The ion, represented as

hydrophobic | A substance that repels water. Hydrophobic substances do not interact favorably with water.

hydrophobic | A substance that repels water. Hydrophobic substances do not interact favorably with water.

hypothesis | A tentative explanation for scientific observations that puts the system being studied into a form that can be tested.

hypothesis | A tentative explanation for scientific observations that puts the system being studied into a form that can be tested.

ideal gas | A hypothetical gaseous substance whose behavior is independent of attractive and repulsive forces.

ideal gas | A hypothetical gaseous substance whose behavior is independent of attractive and repulsive forces.

ideal gas law | A law relating pressure, temperature, volume, and the amount of an ideal gas.

ideal gas law | A law relating pressure, temperature, volume, and the amount of an ideal gas.

ideal solution | A solution that obeys Raoult's law.

ideal solution | A solution that obeys Raoult's law.

indicators | An intensely colored organic molecule whose color changes dramatically depending on the pH of the solution.

indicators | An intensely colored organic molecule whose color changes dramatically depending on the pH of the solution.

induced dipole | A short-lived dipole moment that is created in atoms and nonpolar molecules adjacent to atoms or molecules with an instantaneous dipole moment.

induced dipole | A short-lived dipole moment that is created in atoms and nonpolar molecules adjacent to atoms or molecules with an instantaneous dipole moment.

inert metals | The metals at the bottom of the activity series, which have the least tendency to be oxidized.

inert metals | The metals at the bottom of the activity series, which have the least tendency to be oxidized.

inorganic compounds | An ionic or covalent compound that consists primarily of elements other than carbon and hydrogen.

inorganic compounds | An ionic or covalent compound that consists primarily of elements other than carbon and hydrogen.

instantaneous rate | The reaction rate of a chemical reaction at any given point in time.

instantaneous rate | The reaction rate of a chemical reaction at any given point in time.

integrated rate law | A rate law that expresses the reaction rate in terms of the initial concentration and the measured concentration of one or more reactants ([R]) after a given amount of time

integrated rate law | A rate law that expresses the reaction rate in terms of the initial concentration and the measured concentration of one or more reactants ([R]) after a given amount of time

Intensive properties | A physical property that does not depend on the amount of the substance and physical state at a given temperature and pressure.

Intensive properties | A physical property that does not depend on the amount of the substance and physical state at a given temperature and pressure.

intermediate | A species in a reaction mechanism that does not appear in the balanced chemical equation for the overall reaction.

intermediate | A species in a reaction mechanism that does not appear in the balanced chemical equation for the overall reaction.

intermetallic compounds | An alloy that consists of certain metals that combine in only specific proportions and whose properties are frequently quite different from those of their constituent elements.

intermetallic compounds | An alloy that consists of certain metals that combine in only specific proportions and whose properties are frequently quite different from those of their constituent elements.

interstitial alloy | An alloy formed by inserting smaller atoms into holes in the metal lattice.

interstitial alloy | An alloy formed by inserting smaller atoms into holes in the metal lattice.

interstitial impurity | A point defect that results when an impurity atom occupies an octahedral hole or a tetrahedral hole in the lattice between atoms.

interstitial impurity | A point defect that results when an impurity atom occupies an octahedral hole or a tetrahedral hole in the lattice between atoms.

ion pairs | A cation and anion that are in intimate contact in solution rather than separated by solvent and that migrates in solution as a single unit.

ion pairs | A cation and anion that are in intimate contact in solution rather than separated by solvent and that migrates in solution as a single unit.

ion pumps | A complex assembly of proteins that selectively transports ions across cell membranes toward the side with the higher concentration.

ion pumps | A complex assembly of proteins that selectively transports ions across cell membranes toward the side with the higher concentration.

ion-product constant of liquid water (K_w) | An equilibrium constant for the autoionization of water, $\rightleftharpoons$ + in which the concentration of water is treated as a constant: = =

ion-product constant of liquid water (K_w) | An equilibrium constant for the autoionization of water, $\rightleftharpoons$ + in which the concentration of water is treated as a constant: = =

ionic bonding | A type of chemical bonding in which positively and negatively charged ions are held together by electrostatic forces.

ionic bonding | A type of chemical bonding in which positively and negatively charged ions are held together by electrostatic forces.

ionic liquids | Ionic substances that are liquids at room temperature and pressure and that consist of small, symmetrical anions combined with larger, symmetrical organic cations that prevent the formation of a highly organized structure.

ionic liquids | Ionic substances that are liquids at room temperature and pressure and that consist of small, symmetrical anions combined with larger, symmetrical organic cations that prevent the formation of a highly organized structure.

ionic radius | The radius of a cation or anion.

ionic radius | The radius of a cation or anion.

ionic solid | A solid that consists of positively and negatively charged ions held together by electrostatic forces.

ionic solid | A solid that consists of positively and negatively charged ions held together by electrostatic forces.

ionization energy(I) | The minimum amount of energy needed to remove an electron from the gaseous atom in its ground state:

ionization energy(I) | The minimum amount of energy needed to remove an electron from the gaseous atom in its ground state:

ions | A charged particle produced when one or more electrons is removed from or added to an atom or molecule.

ions | A charged particle produced when one or more electrons is removed from or added to an atom or molecule.

isoelectronic series | A group of ions or atoms and ions that have the same number of electrons and thus the same ground-state electron configuration.

isoelectronic series | A group of ions or atoms and ions that have the same number of electrons and thus the same ground-state electron configuration.

isolated system | A system that can exchange neither energy nor matter with its suroundings.

isolated system | A system that can exchange neither energy nor matter with its suroundings.

joule (J) | The SI unit of energy:

joule (J) | The SI unit of energy:

ketones | A class of organic compounds with the general form RC(O)R’, in which the carbon atom of the carbonyl group is bonded to two alkyl groups (c.f. aldehyde). The alkyl groups may be the same or different.

ketones | A class of organic compounds with the general form RC(O)R’, in which the carbon atom of the carbonyl group is bonded to two alkyl groups (c.f. aldehyde). The alkyl groups may be the same or different.

kinetic energy (*KE*) | Energy due to the motion of an object: where is the mass of the object and is its velocity.

kinetic energy (*KE*) | Energy due to the motion of an object: where is the mass of the object and is its velocity.

kinetic molecular theory of gases | A theory that describes, on the molecular level, why ideal gases behave the way they do.

kinetic molecular theory of gases | A theory that describes, on the molecular level, why ideal gases behave the way they do.

K_p | An equilibrium constant expressed as the ratio of the partial pressures of the products and reactants, each raised to its coefficient in the chemical equation.

K_p | An equilibrium constant expressed as the ratio of the partial pressures of the products and reactants, each raised to its coefficient in the chemical equation.

law of conservation of energy | The total amount of energy in the universe remains constant. Energy can be neither created nor destroyed, but it can be converted from one form to another.

law of conservation of energy | The total amount of energy in the universe remains constant. Energy can be neither created nor destroyed, but it can be converted from one form to another.

law of conservation of mass | In any chemical reaction, the mass of the substances that react equals the mass of the products that are formed.

law of conservation of mass | In any chemical reaction, the mass of the substances that react equals the mass of the products that are formed.

law of conservation of orbitals | A law that states that the number of molecular orbitals produced is the same as the number of atomic orbitals used to create them.

law of conservation of orbitals | A law that states that the number of molecular orbitals produced is the same as the number of atomic orbitals used to create them.

law of definite proportions | A chemical substance always contains the same proportions of elements by mass.

law of definite proportions | A chemical substance always contains the same proportions of elements by mass.

law of mass action | For the general balanced chemical equation the equilibrium constant expression is

law of mass action | For the general balanced chemical equation the equilibrium constant expression is

law of multiple proportions | When two elements form a series of compounds, the ratios of the masses of the second element that are present per gram of the first element can almost always be expressed as the ratios of integers. (The same law holds for the mass ratios of compounds forming a series that contains more than two elements.)

law of multiple proportions | When two elements form a series of compounds, the ratios of the masses of the second element that are present per gram of the first element can almost always be expressed as the ratios of integers. (The same law holds for the mass ratios of compounds forming a series that contains more than two elements.)

Le Châtelier’s principle | If a stress is applied to a system at equilibrium, the composition of the system will change to relieve the applied stress.

Le Châtelier’s principle | If a stress is applied to a system at equilibrium, the composition of the system will change to relieve the applied stress.

leveling effect | The phenomenon that makes the strongest acid that can exist in water. Any species that is a stronger acid than is leveled to the strength of in aqueous solution.

Lewis acid | Any species that can accept a pair of electrons.

Lewis acid | Any species that can accept a pair of electrons.

Lewis electron dot symbols | A system that can be used to predict the number of bonds formed by most elements in their compounds.

Lewis electron dot symbols | A system that can be used to predict the number of bonds formed by most elements in their compounds.

limiting reactant | The reactant that restricts the amount of product obtained in a chemical reaction.

limiting reactant | The reactant that restricts the amount of product obtained in a chemical reaction.

line spectrum | A spectrum in which light of only a certain wavelength is emitted or absorbed, rather than a continuous range of wavelengths.

line spectrum | A spectrum in which light of only a certain wavelength is emitted or absorbed, rather than a continuous range of wavelengths.

linear combinations of atomic orbitals (LCAOs) | Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals).

linear combinations of atomic orbitals (LCAOs) | Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals).

Liquefaction | The condensation of gases into a liquid form.

Liquefaction | The condensation of gases into a liquid form.

liquid crystals | A substance that exhibits phases that have properties intermediate between those of a crystalline solid and a normal liquid and possess long-range molecular order but still flow.

liquid crystals | A substance that exhibits phases that have properties intermediate between those of a crystalline solid and a normal liquid and possess long-range molecular order but still flow.

London dispersion forces | A kind of intermolecular interaction (force) that results from temporary fluctuations in the electron distribution within atoms and nonpolar molecules.

London dispersion forces | A kind of intermolecular interaction (force) that results from temporary fluctuations in the electron distribution within atoms and nonpolar molecules.

lustrous | Having a shiny appearance. Metals are lustrous, whereas nonmetals are not.

lustrous | Having a shiny appearance. Metals are lustrous, whereas nonmetals are not.

macrominerals | Any of the six essential elements (Na, Mg, K, Ca, Cl, and P) that provide essential ions in body fluids and form the major structural components of the body.

macrominerals | Any of the six essential elements (Na, Mg, K, Ca, Cl, and P) that provide essential ions in body fluids and form the major structural components of the body.

magnetic quantum number (m_l) | One of three quantum numbers that describes the orientation of the region of space occupied by an electron with respect to an applied magnetic field.

magnetic quantum number (m_l) | One of three quantum numbers that describes the orientation of the region of space occupied by an electron with respect to an applied magnetic field.

manometers | A device used to measure the pressures of samples of gases contained in an apparatus.

manometers | A device used to measure the pressures of samples of gases contained in an apparatus.

mass number (*A*) | The number of protons and neutrons in the nucleus of an atom of an element.

mass number (*A*) | The number of protons and neutrons in the nucleus of an atom of an element.

matter | Anything that occupies space and has mass.

matter | Anything that occupies space and has mass.

mean free path | The average distance traveled by a molecule between collisions.

mean free path | The average distance traveled by a molecule between collisions.

mechanical work | The energy required to move an object a distance when opposed by a force :

mechanical work | The energy required to move an object a distance when opposed by a force :

Meissner effect | The phenomenon in which a superconductor completely expels a magnetic field from its interior.

Meissner effect | The phenomenon in which a superconductor completely expels a magnetic field from its interior.

melting point | The temperature at which the individual ions in a lattice or the individual molecules in a covalent compound have enough kinetic energy to overcome the attractive forces that hold them together in the solid.

melting point | The temperature at which the individual ions in a lattice or the individual molecules in a covalent compound have enough kinetic energy to overcome the attractive forces that hold them together in the solid.

meniscus | The upper surface of the liquid in a tube.

meniscus | The upper surface of the liquid in a tube.

Metal-matrix composites | A composite that consists of reinforcing fibers embedded in a metal or a metal alloy matrix.

Metal-matrix composites | A composite that consists of reinforcing fibers embedded in a metal or a metal alloy matrix.

metallic solids | A solid that consists of metal atoms held together by metallic bonds.

metallic solids | A solid that consists of metal atoms held together by metallic bonds.

micelles | A spherical or cylindrical aggregate of detergents or soaps in water that minimizes contact between the hydrophobic tails of the detergents or soaps and water.

micelles | A spherical or cylindrical aggregate of detergents or soaps in water that minimizes contact between the hydrophobic tails of the detergents or soaps and water.

midpoint | The point in an acid–base titration at which exactly enough acid (or base) has been added to neutralize one-half of the base (or the acid) originally present:

miscible | Capable of forming a single homogeneous phase, regardless of the proportions with which the substances are mixed.

miscible | Capable of forming a single homogeneous phase, regardless of the proportions with which the substances are mixed.

molality (*m*) | The number of moles of solute present in exactly 1 kg of solvent.

molality (*m*) | The number of moles of solute present in exactly 1 kg of solvent.

molar mass | The mass in grams of 1 mol of a substance.

molar mass | The mass in grams of 1 mol of a substance.

molar volume | The molar mass of an element divided by its density.

molar volume | The molar mass of an element divided by its density.

molarity (M) | A common unit of concentration that is the number of moles of solute present in exactly 1 L of solution

molarity (M) | A common unit of concentration that is the number of moles of solute present in exactly 1 L of solution

mole (mol) | The quantity of a substance that contains the same number of units (e.g., atoms or molecules) as the number of carbon atoms in exactly 12 g of isotopically pure carbon-12.

mole (mol) | The quantity of a substance that contains the same number of units (e.g., atoms or molecules) as the number of carbon atoms in exactly 12 g of isotopically pure carbon-12.

mole fraction (*X*) | The ratio of the number of moles of any component of a mixture to the total number of moles of all species present in the mixture.

mole fraction (*X*) | The ratio of the number of moles of any component of a mixture to the total number of moles of all species present in the mixture.

mole ratio | The ratio of the number of moles of one substance to the number of moles of another, as depicted by a balanced chemical equation.

mole ratio | The ratio of the number of moles of one substance to the number of moles of another, as depicted by a balanced chemical equation.

molecular formula | A representation of a covalent compound that consists of the atomic symbol for each component element (in a prescribed order) accompanied by a subscript indicating the number of atoms of that element in the molecule. The subscript is written only if the number is greater than 1.

molecular formula | A representation of a covalent compound that consists of the atomic symbol for each component element (in a prescribed order) accompanied by a subscript indicating the number of atoms of that element in the molecule. The subscript is written only if the number is greater than 1.

molecular geometry | The arrangement of the bonded atoms in a molecule or a polyatomic ion in space.

molecular geometry | The arrangement of the bonded atoms in a molecule or a polyatomic ion in space.

molecular mass | The sum of the average masses of the atoms in one molecule of a substance, each multiplied by its subscript.

molecular mass | The sum of the average masses of the atoms in one molecule of a substance, each multiplied by its subscript.

molecular orbital theory | A delocalized bonding model in which molecular orbitals are created from the linear combination of atomic orbitals (LCAOs).

molecular orbital theory | A delocalized bonding model in which molecular orbitals are created from the linear combination of atomic orbitals (LCAOs).

Molecular solids | A solid that consists of molecules held together by relatively weak forces, such as dipole-dipole interactions, hydrogen bonds, and London dispersion forces.

Molecular solids | A solid that consists of molecules held together by relatively weak forces, such as dipole-dipole interactions, hydrogen bonds, and London dispersion forces.

molecularity | The number of molecules that collide during any step in a reaction mechanism.

molecularity | The number of molecules that collide during any step in a reaction mechanism.

molten salt | A salt that has been heated to its melting point.

molten salt | A salt that has been heated to its melting point.

monatomic | A species containing a single atom.

monatomic | A species containing a single atom.

monatomic ions | An ion with only a single atom.

monatomic ions | An ion with only a single atom.

***n*-type semiconductor** | A semiconductor that has been doped with an impurity that has more valence electrons than the atoms of the host lattice.

***n*-type semiconductor** | A semiconductor that has been doped with an impurity that has more valence electrons than the atoms of the host lattice.

nanotubes | One of at least four allotropes of carbon that are cylinders of carbon atoms and are intermediate in structure between graphite and the fullerenes.

nanotubes | One of at least four allotropes of carbon that are cylinders of carbon atoms and are intermediate in structure between graphite and the fullerenes.

net ionic equation | A chemical equation that shows only those species that participate in the chemical reaction.

net ionic equation | A chemical equation that shows only those species that participate in the chemical reaction.

neutral solution | A solution in which the total positive charge from all the cations is matched by an identical total negative charge from all the anions.

neutral solution | A solution in which the total positive charge from all the cations is matched by an identical total negative charge from all the anions.

neutrons | A subatomic particle with no charge that resides in the nucleus of almost all atoms.

neutrons | A subatomic particle with no charge that resides in the nucleus of almost all atoms.

noble gases | Any element in group 18 of the periodic table. All are unreactive monatomic gases at room temperature and pressure.

noble gases | Any element in group 18 of the periodic table. All are unreactive monatomic gases at room temperature and pressure.

nodes | The point where the amplitude of a wave is zero.

nodes | The point where the amplitude of a wave is zero.

nonbonding molecular orbitals | A molecular orbital that forms when atomic orbitals or orbital lobes interact only very weakly, creating essentially no change in the electron probability density between the nuclei.

nonbonding molecular orbitals | A molecular orbital that forms when atomic orbitals or orbital lobes interact only very weakly, creating essentially no change in the electron probability density between the nuclei.

nonstoichiometric compounds | A solid that has intrinsically variable stoichiometries without affecting the fundamental structure of the crystal.

nonstoichiometric compounds | A solid that has intrinsically variable stoichiometries without affecting the fundamental structure of the crystal.

nonvolatile liquids | A liquid with a relatively low vapor pressure.

nonvolatile liquids | A liquid with a relatively low vapor pressure.

normal boiling point | The temperature at which a substance boils at a pressure of 1 atm.

normal boiling point | The temperature at which a substance boils at a pressure of 1 atm.

nucleus | The central core of an atom where protons and any neutrons reside.

nucleus | The central core of an atom where protons and any neutrons reside.

octane rating | A measure of a fuel's ability to burn in a combustion engine without knocking or pinging (indications of premature combustion). The higher the octane rating, the higher quality the fuel.

octane rating | A measure of a fuel's ability to burn in a combustion engine without knocking or pinging (indications of premature combustion). The higher the octane rating, the higher quality the fuel.

octaves | A group of seven elements, corresponding to the horizontal rows in the main group elements (not counting the noble gases, which were unknown at the time).

octaves | A group of seven elements, corresponding to the horizontal rows in the main group elements (not counting the noble gases, which were unknown at the time).

octet rule | The tendency for atoms to lose, gain, or share electrons to reach a total of eight valence electrons.

octet rule | The tendency for atoms to lose, gain, or share electrons to reach a total of eight valence electrons.

orbital energies | A particular energy associated with a given set of quantum numbers.

orbital energies | A particular energy associated with a given set of quantum numbers.

osmosis | The net flow of solvent through a semipermeable membrane.

osmosis | The net flow of solvent through a semipermeable membrane.

osmotic pressure (Π) | The pressure difference between the two sides of a semipermeable membrane that separates a pure solvent from a solution prepared from the same solvent.

osmotic pressure (Π) | The pressure difference between the two sides of a semipermeable membrane that separates a pure solvent from a solution prepared from the same solvent.

overall chemical equation | A chemical equation that shows all the reactants and products as undissociated, electrically neutral compounds.

overall chemical equation | A chemical equation that shows all the reactants and products as undissociated, electrically neutral compounds.

overlapping bands | Molecular orbitals derived from two or more different kinds of valence electrons that have similar energies.

overlapping bands | Molecular orbitals derived from two or more different kinds of valence electrons that have similar energies.

overtones | The vibration of a standing wave that is higher in energy than the fundamental vibration.

overtones | The vibration of a standing wave that is higher in energy than the fundamental vibration.

oxidation | The loss of one or more electrons in a chemical reaction. The substance that loses electrons is said to be oxidized.

oxidation | The loss of one or more electrons in a chemical reaction. The substance that loses electrons is said to be oxidized.

oxidation state | The charge that each atom in a compound would have if all its bonding electrons were transferred to the atom with the greater attraction for electrons.

oxidation state | The charge that each atom in a compound would have if all its bonding electrons were transferred to the atom with the greater attraction for electrons.

oxidation state method | A procedure for balancing oxidation–reduction (redox) reactions in which the overall reaction is conceptually separated into two parts: an oxidation and a reduction.

oxidation state method | A procedure for balancing oxidation–reduction (redox) reactions in which the overall reaction is conceptually separated into two parts: an oxidation and a reduction.

oxidation–reduction reactions | A chemical reaction that exhibits a change in the oxidation states of one or more elements in the reactants that has the general form oxidant + reductant → reduced oxidant + oxidized reductant.

oxidation–reduction reactions | A chemical reaction that exhibits a change in the oxidation states of one or more elements in the reactants that has the general form oxidant + reductant → reduced oxidant + oxidized reductant.

oxoacids | An acid in which the dissociable ion is attached to an oxygen atom of a polyatomic anion.

oxoacids | An acid in which the dissociable ion is attached to an oxygen atom of a polyatomic anion.

Ozone | An unstable form of oxygen that consists of three oxygen atoms bonded together (O_3). A layer of ozone in the stratosphere helps protect the plants and animals on earth from harmful ultraviolet radiation. Ozone is responsible for the pungent smell we associate with lightning discharges and electric motors. It is also toxic.

Ozone | An unstable form of oxygen that consists of three oxygen atoms bonded together (O_3). A layer of ozone in the stratosphere helps protect the plants and animals on earth from harmful ultraviolet radiation. Ozone is responsible for the pungent smell we associate with lightning discharges and electric motors. It is also toxic.

ozone layer | A concentration of ozone in the stratosphere (about 10^{15} ozone molecules per liter) that acts as a protective screen, absorbing ultraviolet light that would otherwise reach the surface of the earth, where it would harm plants and animals.

ozone layer | A concentration of ozone in the stratosphere (about 10^{15} ozone molecules per liter) that acts as a protective screen, absorbing ultraviolet light that would otherwise reach the surface of the earth, where it would harm plants and animals.

***p*-type semiconductor** | A semiconductor that has been doped with an impurity that has fewer valence electrons than the atoms of the host lattice.

***p*-type semiconductor** | A semiconductor that has been doped with an impurity that has fewer valence electrons than the atoms of the host lattice.

partial pressure | The pressure a gas in a mixture would exert if it were the only one present (at the same temperature and volume).

partial pressure | The pressure a gas in a mixture would exert if it were the only one present (at the same temperature and volume).

parts per billion (ppb) | Micrograms of solute per kilogram of solvent.

parts per billion (ppb) | Micrograms of solute per kilogram of solvent.

parts per thousand (ppt) | Grams of solute per kilogram of solvent, primarily used in the health sciences.

parts per thousand (ppt) | Grams of solute per kilogram of solvent, primarily used in the health sciences.

pascal (Pa) | The SI unit for pressure. The pascal is newtons per square meter:

pascal (Pa) | The SI unit for pressure. The pascal is newtons per square meter:

Pauli exclusion principle | A principle stating that no two electrons in an atom can have the same value of all four quantum numbers.

Pauli exclusion principle | A principle stating that no two electrons in an atom can have the same value of all four quantum numbers.

percent composition | The percentage of each element present in a pure substance. With few exceptions, the percent composition of a chemical compound is constant (see law of definite proportions).

percent composition | The percentage of each element present in a pure substance. With few exceptions, the percent composition of a chemical compound is constant (see law of definite proportions).

percent yield | The ratio of the actual yield of a reaction to the theoretical yield multiplied by 100 to give a percentage.

percent yield | The ratio of the actual yield of a reaction to the theoretical yield multiplied by 100 to give a percentage.

periodic table | A chart of the chemical elements arranged in rows of increasing atomic number so that the elements in each column (group) have similar chemical properties.

periodic table | A chart of the chemical elements arranged in rows of increasing atomic number so that the elements in each column (group) have similar chemical properties.

perovskite structure | A structure that consists of a bcc array of two metal ions, with one set (M) located at the corners of the cube, and the other set (M′) in the centers of the cube.

perovskite structure | A structure that consists of a bcc array of two metal ions, with one set (M) located at the corners of the cube, and the other set (M′) in the centers of the cube.

pH | The negative base-10 logarithm of the hydrogen ion concentration:

pH | The negative base-10 logarithm of the hydrogen ion concentration:

pH scale | A logarithmic scale used to express the hydrogen ion concentration of a solution, making it possible to describe acidity or basicity quantitatively.

pH scale | A logarithmic scale used to express the hydrogen ion concentration of a solution, making it possible to describe acidity or basicity quantitatively.

phase changes | A change of state that occurs when any of the three forms of matter (solids, liquids, and gases) is converted to either of the other two.

phase changes | A change of state that occurs when any of the three forms of matter (solids, liquids, and gases) is converted to either of the other two.

phase diagram | A graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system.

phase diagram | A graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system.

photoelectric effect | A phenomenon in which electrons are ejected from the surface of a metal that has been exposed to light.

photoelectric effect | A phenomenon in which electrons are ejected from the surface of a metal that has been exposed to light.

photons | A quantum of radiant energy, each of which possesses a particular energy given by

photons | A quantum of radiant energy, each of which possesses a particular energy given by

physical change | A change of state that does not affect the chemical composition of a substance.

physical change | A change of state that does not affect the chemical composition of a substance.

pi star (π*) orbital | An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel atomic orbitals, creating a nodal plane perpendicular to the internuclear axis.

pi star (π*) orbital | An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel atomic orbitals, creating a nodal plane perpendicular to the internuclear axis.

pinning | A process that increases the mechanical strength of a material by introducing multiple defects into a material so that the presence of one defect prevents the motion of another.

pinning | A process that increases the mechanical strength of a material by introducing multiple defects into a material so that the presence of one defect prevents the motion of another.

Plastic | The property of a material that allows it to be molded into almost any shape.

Plastic | The property of a material that allows it to be molded into almost any shape.

pnicogens | The elements in group 15 of the periodic table.

pnicogens | The elements in group 15 of the periodic table.

polar bond | A chemical bond in which there is an unequal distribution of charge between the bonding atoms.

polar bond | A chemical bond in which there is an unequal distribution of charge between the bonding atoms.

polar covalent bonds | A covalent bond in which the electrons are shared unequally between the bonded atoms.

polar covalent bonds | A covalent bond in which the electrons are shared unequally between the bonded atoms.

polarizability | The ease of deformation of the electron distribution in an atom or molecule.

polarizability | The ease of deformation of the electron distribution in an atom or molecule.

polyatomic | Molecules that contain more than two atoms.

polyatomic | Molecules that contain more than two atoms.

Polyatomic ions | A group of two or more atoms that has a net electrical charge.

Polyatomic ions | A group of two or more atoms that has a net electrical charge.

polymer-matrix composite | A compositie that consists of reinforcing fibers embedded in a polymer matrix.

polymer-matrix composite | A compositie that consists of reinforcing fibers embedded in a polymer matrix.

precipitate | The insoluble product that forms in a precipitation reaction.

precipitate | The insoluble product that forms in a precipitation reaction.

precise | Multiple measurements give nearly identical values.

precise | Multiple measurements give nearly identical values.

pressure(P) | The amount of force exerted on a given area of surface:

pressure(P) | The amount of force exerted on a given area of surface:

principal quantum number (n) | One of three quantum numbers that tells the average relative distance of an electron from the nucleus.

principal quantum number (n) | One of three quantum numbers that tells the average relative distance of an electron from the nucleus.

principal shell | All the wave functions that have the same value of because those electrons have similar average distances from the nucleus.

principal shell | All the wave functions that have the same value of because those electrons have similar average distances from the nucleus.

product(s) | The final compound(s) produced in a chemical reaction.

product(s) | The final compound(s) produced in a chemical reaction.

promotion | The excitation of an electron from a filled atomic orbital to an empty or valence orbital.

promotion | The excitation of an electron from a filled atomic orbital to an empty or valence orbital.

pseudo noble gas configurations | The and similar electron configurations that are particularly stable and are often encountered in the heavier -block elements.

pseudo noble gas configurations | The and similar electron configurations that are particularly stable and are often encountered in the heavier -block elements.

pyrolysis | A high-temperature decomposition reaction that can be used to form fibers of synthetic polymers.

pyrolysis | A high-temperature decomposition reaction that can be used to form fibers of synthetic polymers.

quantum | The smallest possible unit of energy. Energy can be gained or lost only in integral multiples of a quantum.

quantum | The smallest possible unit of energy. Energy can be gained or lost only in integral multiples of a quantum.

quantum mechanics | A theory developed by Erwin Schrödinger that describes the energies and spatial distributions of electrons in atoms and molecules.

quantum mechanics | A theory developed by Erwin Schrödinger that describes the energies and spatial distributions of electrons in atoms and molecules.

R | The abbreviation used for alkyl groups and aryl groups in general formulas and structures.

R | The abbreviation used for alkyl groups and aryl groups in general formulas and structures.

radicals | Species that have one or more unpaired valence electrons.

radicals | Species that have one or more unpaired valence electrons.

radioactivity | The spontaneous emission of energy rays (radiation) by matter.

radioactivity | The spontaneous emission of energy rays (radiation) by matter.

Raoult's law | An equation that quantifies the relationship between solution composition and vapor pressure:

Raoult's law | An equation that quantifies the relationship between solution composition and vapor pressure:

rate constant | A proportionality constant whose value is characteristic of the reaction and the reaction conditions and whose numerical value does not change as the reaction progresses under a given set of conditions.

rate constant | A proportionality constant whose value is characteristic of the reaction and the reaction conditions and whose numerical value does not change as the reaction progresses under a given set of conditions.

rate laws | Mathematical expressions that describe the relationships between reactant rates and reactant concentrations in a chemical reaction.

rate laws | Mathematical expressions that describe the relationships between reactant rates and reactant concentrations in a chemical reaction.

rate-determining step | The slowest step in a reaction mechanism.

rate-determining step | The slowest step in a reaction mechanism.

reaction mechanisms | The sequence of events that occur at the molecular level during a reaction.

reaction mechanisms | The sequence of events that occur at the molecular level during a reaction.

reaction order | Numbers that indicate the degree to which the reaction rate depends on the concentration of each reactant.

reaction order | Numbers that indicate the degree to which the reaction rate depends on the concentration of each reactant.

reaction quotient (Q) | A quantity derived from a set of values measured at any time during the reaction of any mixture of reactants and products, regardless of whether the system is at equilibrium: for the general balanced chemical equation

reaction quotient (Q) | A quantity derived from a set of values measured at any time during the reaction of any mixture of reactants and products, regardless of whether the system is at equilibrium: for the general balanced chemical equation

reaction quotient (Q_p) | A quantity derived from a set of values measured at any time during the reaction of any mixture of reactants and products in the gas phase, regardless of whether the system is at equilibrium: for the general balanced chemical equation

reaction quotient (Q_p) | A quantity derived from a set of values measured at any time during the reaction of any mixture of reactants and products in the gas phase, regardless of whether the system is at equilibrium: for the general balanced chemical equation

reaction rates | The changes in concentrations of reactants and products with time.

reaction rates | The changes in concentrations of reactants and products with time.

reductants (or reducing agents) | A compound that is capable of donating electrons; thus it is oxidized.

reductants (or reducing agents) | A compound that is capable of donating electrons; thus it is oxidized.

reduction | The gain of one or more electrons in a chemical reaction. The substance that gains electrons is said to be reduced.

reduction | The gain of one or more electrons in a chemical reaction. The substance that gains electrons is said to be reduced.

reforming | The second process used in petroleum refining, which is the chemical conversion of straight-chain alkanes to either branched-chain alkanes or mixtures of aromatic hydrocarbons.

reforming | The second process used in petroleum refining, which is the chemical conversion of straight-chain alkanes to either branched-chain alkanes or mixtures of aromatic hydrocarbons.

resonance structures | A Lewis electron structure that has different arrangements of electrons around atoms whose positions do not change.

resonance structures | A Lewis electron structure that has different arrangements of electrons around atoms whose positions do not change.

reverse osmosis | A process that uses the application of an external pressure greater than the osmotic pressure of a solution to reverse the flow of solvent through the semipermeable membrane.

reverse osmosis | A process that uses the application of an external pressure greater than the osmotic pressure of a solution to reverse the flow of solvent through the semipermeable membrane.

root mean square (rms) speed(v_{rms}) | The speed of a gas particle that has average kinetic energy.

root mean square (rms) speed(v_{rms}) | The speed of a gas particle that has average kinetic energy.

salt | The general term for any ionic substance that does not have as the anion or as the cation.

salt | The general term for any ionic substance that does not have as the anion or as the cation.

saturated | A solution with the maximum possible amount of a solute under a given set of conditions.

saturated | A solution with the maximum possible amount of a solute under a given set of conditions.

Schottky defects | A coupled pair of vacancies—one cation and one anion—that maintains the electrical neutrality of an ionic solid.

Schottky defects | A coupled pair of vacancies—one cation and one anion—that maintains the electrical neutrality of an ionic solid.

scientific method | The procedure that scientists use to search for answers to questions and solutions to problems.

scientific method | The procedure that scientists use to search for answers to questions and solutions to problems.

scientific notation | A system that expresses numbers in the form N × 10^n, where N is greater than or equal to 1 and less than 10 ($1 \leq N < 10$) and n is an integer that can be either positive or negative ($10^0 = 1$). The purpose of scientific notation is to simplify the manipulation of numbers with large or small magnitudes.

scientific notation | A system that expresses numbers in the form N × 10^n, where N is greater than or equal to 1 and less than 10 ($1 \leq N < 10$) and n is an integer that can be either positive or negative ($10^0 = 1$). The purpose of scientific notation is to simplify the manipulation of numbers with large or small magnitudes.

second-order reaction | A reaction whose rate is proportional to the square of the concentration of the reactant (for a reaction with the general form $2A \rightarrow$ products) or is proportional to the product of the concentrations of two reactants (for a reaction with the general form $A + B \rightarrow$ products).

second-order reaction | A reaction whose rate is proportional to the square of the concentration of the reactant (for a reaction with the general form $2A \rightarrow$ products) or is proportional to the product of the concentrations of two reactants (for a reaction with the general form $A + B \rightarrow$ products).

seed crystal | A solid sample of a substance that can be added to a supercooled liquid or a supersaturated solution to help induce crystallization.

seed crystal | A solid sample of a substance that can be added to a supercooled liquid or a supersaturated solution to help induce crystallization.

seed crystal | A solid sample of a substance that can be added to a supercooled liquid or a supersaturated solution to help induce crystallization.

seed crystal | A solid sample of a substance that can be added to a supercooled liquid or a supersaturated solution to help induce crystallization.

semiconductors | A substance such as Si and Ge that has a conductivity between that of metals and insulators.

semiconductors | A substance such as Si and Ge that has a conductivity between that of metals and insulators.

semimetals | Any element that lies adjacent to the zigzag line in the periodic table that runs from boron to astatine. Semimetals (also called metalloids) exhibit properties intermediate between those of metals and nonmetals.

semimetals | Any element that lies adjacent to the zigzag line in the periodic table that runs from boron to astatine. Semimetals (also called metalloids) exhibit properties intermediate between those of metals and nonmetals.

sigma (σ) orbital | A bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry.

sigma (σ) orbital | A bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry.

sigma star (σ*) orbital | An antibonding molecular orbital in which there is a region of zero electron probability (a nodal plane) perpendicular to the internuclear axis.

sigma star (σ*) orbital | An antibonding molecular orbital in which there is a region of zero electron probability (a nodal plane) perpendicular to the internuclear axis.

significant figures | Numbers that describe the value without exaggerating the degree to which it is known to be accurate.

significant figures | Numbers that describe the value without exaggerating the degree to which it is known to be accurate.

single-displacement reactions | A chemical reaction in which an ion in solution is displaced through oxidation of a metal.

single-displacement reactions | A chemical reaction in which an ion in solution is displaced through oxidation of a metal.

sintering | A process that fuses the grains of a ceramic into a dense, strong material. Sintering is used to produce high-strength ceramics.

sintering | A process that fuses the grains of a ceramic into a dense, strong material. Sintering is used to produce high-strength ceramics.

sodium chloride structure | The solid structure that results when the octahedral holes of an fcc lattice of anions are filled with cations.

sodium chloride structure | The solid structure that results when the octahedral holes of an fcc lattice of anions are filled with cations.

sol-gel process | A process used to manufacture ceramics by producing fine powders of ceramic oxides with uniformly sized particles.

sol-gel process | A process used to manufacture ceramics by producing fine powders of ceramic oxides with uniformly sized particles.

solid electrolytes | A solid material with a very high electrical conductivity.

solid electrolytes | A solid material with a very high electrical conductivity.

solubility | A measure of the how much of a solid substance remains dissolved in a given amount of a specified liquid at a specified temperature and pressure.

solubility | A measure of the how much of a solid substance remains dissolved in a given amount of a specified liquid at a specified temperature and pressure.

solutions | A homogeneous mixture of two or more substances in which the substances present in lesser amounts (the solutes) are dispersed uniformly throughout the substance present in greater amount (the solvent).

***sp* hybrid orbital** | The two equivalent hybrid orbitals that result when one orbital and one orbital are combined (hybridized). The two hybrid orbitals are oriented at 180° from each other. They are equivalent in energy, and their energy is between the energy values associated with pure and pure orbitals.

***sp* hybrid orbital** | The two equivalent hybrid orbitals that result when one orbital and one orbital are combined (hybridized). The two hybrid orbitals are oriented at 180° from each other. They are equivalent in energy, and their energy is between the energy values associated with pure and pure orbitals.

sp^2 hybrid atomic orbitals | The three equivalent hybrid orbitals that result when one orbital and two orbitals are combined (hybridized). The three hybrid orbitals are oriented in a plane at 120° from each other. They are equivalent in energy, and their energy is between the energy values associated with pure and pure orbitals.

sp^2 hybrid atomic orbitals | The three equivalent hybrid orbitals that result when one orbital and two orbitals are combined (hybridized). The three hybrid orbitals are oriented in a plane at 120° from each other. They are equivalent in energy, and their energy is between the energy values associated with pure and pure orbitals.

sp^3 hybrid atomic orbitals | The four equivalent hybrid orbitals that result when one orbital and three orbitals are combined (hybridized). The four hybrid orbitals point at the vertices of a tetrahedron, so they are oriented at 109.5° from each other. They are equivalent in energy, and their energy is between the energy values associated with pure and pure orbitals.

sp^3 hybrid atomic orbitals | The four equivalent hybrid orbitals that result when one orbital and three orbitals are combined (hybridized). The four hybrid orbitals point at the vertices of a tetrahedron, so they are oriented at 109.5° from each other. They are equivalent in energy, and their energy is between the energy values associated with pure and pure orbitals.

sp^3d hybrid orbitals | The five hybrid orbitals that result when one three and one orbitals are combined (hybridized).

sp^3d hybrid orbitals | The five hybrid orbitals that result when one three and one orbitals are combined (hybridized).

sp^3d^2 hybrid orbitals | The six equivalent hybrid orbitals that result when one , three , and two orbitals are combined (hybridized).

sp^3d^2 hybrid orbitals | The six equivalent hybrid orbitals that result when one , three , and two orbitals are combined (hybridized).

specific heat (C_s) | The amount of energy needed to increase the temperature of 1 g of a substance by 1°C. The units of are

specific heat (C_s) | The amount of energy needed to increase the temperature of 1 g of a substance by 1°C. The units of are

specific heat (C_s) | The number of joules required to raise the temperature of 1 g of a substance by 1°C.

specific heat (C_s) | The number of joules required to raise the temperature of 1 g of a substance by 1°C.

speed (v) | The distance traveled by a wave per unit time.

speed (v) | The distance traveled by a wave per unit time.

speed of light (c) | The speed with which all forms of electromagnetic radiation travel in a vacuum.

speed of light (c) | The speed with which all forms of electromagnetic radiation travel in a vacuum.

standard enthalpies of formation () | The enthalpy change for the formation of 1 mol of a compound from its component elements when the component elements are each in their standard states. The standard enthalpy of formation of any element in its most stable form is zero by definition.

standard enthalpies of formation () | The enthalpy change for the formation of 1 mol of a compound from its component elements when the component elements are each in their standard states. The standard enthalpy of formation of any element in its most stable form is zero by definition.

standard enthalpy of reaction () | The enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard state.

standard enthalpy of reaction () | The enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard state.

standard molar volume | The volume of 1 mol of an ideal gas at STP (0°C and 1 atm pressure), which is 22.41 L.

standard molar volume | The volume of 1 mol of an ideal gas at STP (0°C and 1 atm pressure), which is 22.41 L.

standard solution | A solution whose concentration is precisely known.

standard solution | A solution whose concentration is precisely known.

standard temperature and pressure (STP) | The conditions 0°C (273.15 K) and 1 atm pressure for a gas.

standard temperature and pressure (STP) | The conditions 0°C (273.15 K) and 1 atm pressure for a gas.

state function | A property of a system whose magnitude depends on only the present state of the system, not its previous history.

state function | A property of a system whose magnitude depends on only the present state of the system, not its previous history.

steric factor (p) | The fraction of orientations of particles that result in a chemical reaction.

steric factor (p) | The fraction of orientations of particles that result in a chemical reaction.

stock solution | A commercially prepared solution of known concentration.

stock solution | A commercially prepared solution of known concentration.

stoichiometric quantity | The amount of product or reactant specified by the coefficients in a balanced chemical equation.

stoichiometric quantity | The amount of product or reactant specified by the coefficients in a balanced chemical equation.

strong electrolytes | An electrolyte that dissociates completely into ions when dissolved in water, thus producing an aqueous solution that conducts electricity very well.

strong electrolytes | An electrolyte that dissociates completely into ions when dissolved in water, thus producing an aqueous solution that conducts electricity very well.

structural formulas | A representation of a molecule that shows which atoms are bonded to one another and, in some cases, the approximate arrangement of atoms in space.

structural formulas | A representation of a molecule that shows which atoms are bonded to one another and, in some cases, the approximate arrangement of atoms in space.

subshell | A group of wave functions that have the same values of and

subshell | A group of wave functions that have the same values of and

substitutional impurity | A point defect that results when an impurity atom occupies a normal lattice site.

substitutional impurity | A point defect that results when an impurity atom occupies a normal lattice site.

substrate | The reactant in an enzyme-catalyzed reaction.

substrate | The reactant in an enzyme-catalyzed reaction.

Superalloys | A high-strength alloy based on cobalt, nickel, and iron, often of complex composition, that is used in applications that require mechanical strength, high surface stability, and resistance to high temperatures.

Superalloys | A high-strength alloy based on cobalt, nickel, and iron, often of complex composition, that is used in applications that require mechanical strength, high surface stability, and resistance to high temperatures.

supercritical fluid | The single, dense fluid phase that exists above the critical temperature of a substance.

supercritical fluid | The single, dense fluid phase that exists above the critical temperature of a substance.

superheated liquid | An unstable liquid at a temperature and pressure at which it should be a gas.

superheated liquid | An unstable liquid at a temperature and pressure at which it should be a gas.

surface tension | The energy required to increase the surface area of a liquid by a certain amount. Surface tension is measured in units of energy per area (e.g.,).

surface tension | The energy required to increase the surface area of a liquid by a certain amount. Surface tension is measured in units of energy per area (e.g.,).

surfactants | Substances (surface-active agents), such as soaps and detergents, that disrupt the attractive intermolecular interactions between molecules of a polar liquid, thereby reducing the surface tension of the liquid.

surfactants | Substances (surface-active agents), such as soaps and detergents, that disrupt the attractive intermolecular interactions between molecules of a polar liquid, thereby reducing the surface tension of the liquid.

surroundings | All the universe that is not the system; that is, system + surroundings = universe.

surroundings | All the universe that is not the system; that is, system + surroundings = universe.

Système internationale d'unités (or SI) | A system of units based on metric units that requires measurements to be expressed in decimal form. There are seven base units in the SI system.

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tetrahedral holes | One of two kinds of holes in a face-centered cubic array of atoms or ions (the other is an octahedral hole). Tetrahedral holes are located between an atom at a corner and the three atoms at the centers of the adjacent faces of the face-centered cubic unit cell. An atom or ion in a tetrahedral hole has a coordination number of 4.

tetrahedral holes | One of two kinds of holes in a face-centered cubic array of atoms or ions (the other is an octahedral hole). Tetrahedral holes are located between an atom at a corner and the three atoms at the centers of the adjacent faces of the face-centered cubic unit cell. An atom or ion in a tetrahedral hole has a coordination number of 4.

theoretical yield | The maximum amount of product that can be formed from the reactants in a chemical reaction, which theoretically is the amount of product that would be obtained if the reaction occurred perfectly and the method of purifying the product were 100% efficient.

theoretical yield | The maximum amount of product that can be formed from the reactants in a chemical reaction, which theoretically is the amount of product that would be obtained if the reaction occurred perfectly and the method of purifying the product were 100% efficient.

theory | A statement that attempts to explain *why* nature behaves the way it does.

theory | A statement that attempts to explain *why* nature behaves the way it does.

thermochemistry | A branch of chemistry that describes the energy changes that occur during chemical reactions.

thermochemistry | A branch of chemistry that describes the energy changes that occur during chemical reactions.

thermodynamic control | The altering of reaction conditions so that a single desired product or set of products is present in significant quantities at equilibrium.

thermodynamic control | The altering of reaction conditions so that a single desired product or set of products is present in significant quantities at equilibrium.

titration curve | A plot of the pH of the solution being titrated versus the amount of acid or base (of known concentration) added.

transition elements | Any element in groups 3–12 in the periodic table. All of the transition elements are metals.

transition elements | Any element in groups 3–12 in the periodic table. All of the transition elements are metals.

transition metals | Any element in groups 3–12 in the periodic table. All of the transition elements are metals.

transition metals | Any element in groups 3–12 in the periodic table. All of the transition elements are metals.

transition state | Also called the activated complex, the arrangement of atoms that first forms when molecules are able to overcome the activation energy and react.

transition state | Also called the activated complex, the arrangement of atoms that first forms when molecules are able to overcome the activation energy and react.

transmutation | The process of converting one element to another.

transmutation | The process of converting one element to another.

triads | A set of three elements that have similar properties.

triads | A set of three elements that have similar properties.

triple bond | A chemical bond formed when two atoms share three pairs of electrons.

triple bond | A chemical bond formed when two atoms share three pairs of electrons.

triple point | The point in a phase diagram where the solid/liquid, liquid/gas, and solid/gas lines intersect; it represents the only combination of temperature and pressure at which all three phases are in equilibrium and can therefore exist simultaneously.

triple point | The point in a phase diagram where the solid/liquid, liquid/gas, and solid/gas lines intersect; it represents the only combination of temperature and pressure at which all three phases are in equilibrium and can therefore exist simultaneously.

triprotic acid | A compound that can donate three protons per molecule in separate steps.

triprotic acid | A compound that can donate three protons per molecule in separate steps.

troposphere | The lowest layer of the atmosphere, the troposphere extends from earth's surface to an altitude of about 11–13 km (7–8 miles). The temperature of the troposphere decreases steadily with increasing altitude.

troposphere | The lowest layer of the atmosphere, the troposphere extends from earth's surface to an altitude of about 11–13 km (7–8 miles). The temperature of the troposphere decreases steadily with increasing altitude.

Tyndall effect | The phenomenon of scattering a beam of visible light.

Tyndall effect | The phenomenon of scattering a beam of visible light.

ultraviolet light | High-energy radiation that cannot be detected by the human eye but can cause a wide variety of chemical reactions that are harmful to organisms.

ultraviolet light | High-energy radiation that cannot be detected by the human eye but can cause a wide variety of chemical reactions that are harmful to organisms.

unit cell | The smallest repeating unit of a crystal lattice.

unit cell | The smallest repeating unit of a crystal lattice.

vacancy | A point defect that consists of a single atom missing from a site in a crystal.

vacancy | A point defect that consists of a single atom missing from a site in a crystal.

valence bond theory | A localized bonding model that assumes that the strength of a covalent bond is proportional to the amount of overlap between atomic orbitals and that an atom can use different combinations of atomic orbitals (hybrids) to maximize the overlap between bonded atoms.

valence bond theory | A localized bonding model that assumes that the strength of a covalent bond is proportional to the amount of overlap between atomic orbitals and that an atom can use different combinations of atomic orbitals (hybrids) to maximize the overlap between bonded atoms.

valence electrons | Electrons in the outermost shell of an atom.

valence electrons | Electrons in the outermost shell of an atom.

valence-shell electron-pair repulsion (VSEPR) model | A model used to predict the shapes of many molecules and polyatomic ions, based on the idea that the lowest-energy arrangement for a compound is the one in which its electron pairs (bonding and nonbonding) are as far apart as possible.

valence-shell electron-pair repulsion (VSEPR) model | A model used to predict the shapes of many molecules and polyatomic ions, based on the idea that the lowest-energy arrangement for a compound is the one in which its electron pairs (bonding and nonbonding) are as far apart as possible.

van der Waals atomic radius(r_{vdW}) | Half the internuclear distance between two nonbonded atoms in the solid.

van der Waals atomic radius(r_{vdW}) | Half the internuclear distance between two nonbonded atoms in the solid.

van der Waals equation | A modification of the ideal gas law designed to describe the behavior of real gases by explicitly including the effects of molecular volume and intermolecular forces.

van der Waals equation | A modification of the ideal gas law designed to describe the behavior of real gases by explicitly including the effects of molecular volume and intermolecular forces.

van der Waals forces | The intermolecular forces known as dipole–dipole interactions and London dispersion forces.

van der Waals forces | The intermolecular forces known as dipole–dipole interactions and London dispersion forces.

van't Hoff factor(i) | The ratio of the apparent number of particles in solution to the number predicted by the stoichiometry of the salt.

van't Hoff factor(i) | The ratio of the apparent number of particles in solution to the number predicted by the stoichiometry of the salt.

vapor pressure | The pressure created over a liquid by the molecules of a liquid substance that have enough kinetic energy to escape to the vapor phase.

vapor pressure | The pressure created over a liquid by the molecules of a liquid substance that have enough kinetic energy to escape to the vapor phase.

Viscosity (η) | The resistance of a liquid to flow.

Viscosity (η) | The resistance of a liquid to flow.

volume | The amount of space occupied by a sample of matter.

volume | The amount of space occupied by a sample of matter.

waters of hydration | The loosely bound water molecules in hydrate compounds. These waters of hydration can often be removed by simply heating the compound.

waters of hydration | The loosely bound water molecules in hydrate compounds. These waters of hydration can often be removed by simply heating the compound.

wave | A periodic oscillation that transmits energy through space.

wave | A periodic oscillation that transmits energy through space.

wave function (Ψ) | A mathematical function that relates the location of an electron at a given point in space to the amplitude of its wave, which corresponds to its energy.

wave function (Ψ) | A mathematical function that relates the location of an electron at a given point in space to the amplitude of its wave, which corresponds to its energy.

wave–particle duality | A principle that matter and energy have properties typical of both waves and particles.

wave–particle duality | A principle that matter and energy have properties typical of both waves and particles.

weak bases | A base in which only a fraction of the molecules react with water to produce and the corresponding cation.

weak bases | A base in which only a fraction of the molecules react with water to produce and the corresponding cation.

weak electrolytes | A compound that produces relatively few ions when dissolved in water, thus producing an aqueous solution that conducts electricity poorly.

weak electrolytes | A compound that produces relatively few ions when dissolved in water, thus producing an aqueous solution that conducts electricity poorly.

weight | A force caused by the gravitational attraction that operates on an object. The weight of an object depends on its location (c.f. mass).

weight | A force caused by the gravitational attraction that operates on an object. The weight of an object depends on its location (c.f. mass).

Work hardening | The practice of introducing a dense network of dislocations throughout a solid, making it very tough and hard.

Work hardening | The practice of introducing a dense network of dislocations throughout a solid, making it very tough and hard.

x-ray diffraction | An technique used to obtain information about the structures of crystalline substances by using x-rays.

x-ray diffraction | An technique used to obtain information about the structures of crystalline substances by using x-rays.

zeroth-order reaction | A reaction whose rate is independent of concentration.

zeroth-order reaction | A reaction whose rate is independent of concentration.

zinc blende structure | The solid structure that results when half of the tetrahedral holes in an fcc lattice of anions are filled with cations with a 1:1 cation:anion ratio and a coordination number of 4.

zinc blende structure | The solid structure that results when half of the tetrahedral holes in an fcc lattice of anions are filled with cations with a 1:1 cation:anion ratio and a coordination number of 4.

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