CHEM 202: GENERAL CHEMISTRY II OER

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CHEM 202 Text

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TABLE OF CONTENTS

1: Introduction to Organic Chemistry

2: Coordination Chemistry of Transition Metals

3: Chemical Kinetics

4: Chemical Equilibrium

5: Acid-Base Equilibria

6: Acid-Base Equilibria in Mixtures

7: Solubility and Complex-Ion Equilibria

8: Thermodynamics

9: Electrochemistry

10: Nuclear Chemistry

Index

Glossary

Detailed Licensing

Licensing

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CHAPTER OVERVIEW

1: Introduction to Organic Chemistry

1.1: General Characteristics of Organic Molecules

Learning Objectives

- To recognize the composition and properties typical of organic and inorganic compounds.

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from "organized" (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate (AgOCN) and ammonium chloride (NH_4Cl), expecting to get ammonium cyanate (NH_4OCN). What he expected is described by the following equation.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{1.1.1}$$

Instead, he found the product to be urea (NH_2CONH_2), a well-known organic material readily isolated from urine. This result led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory was gradually discarded as chemists learned that they could make many organic compounds in the laboratory.

Today **organic chemistry** is the study of the chemistry of the carbon compounds, and **inorganic chemistry** is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

> The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table 1.1.1.

Table 1.1.1: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane	Inorganic	NaCl
low melting points	−95°C	high melting points	801°C
low boiling points	69°C	high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline	greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable	nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive	aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds	exhibit ionic bonding	ionic bonds

Keep in mind, however, that there are exceptions to every category in this table. To further illustrate typical differences among organic and inorganic compounds, Table 1.1.1 also lists properties of the inorganic compound sodium chloride (common table salt, NaCl) and the organic compound hexane (C_6H_{14}), a solvent that is used to extract soybean oil from soybeans (among other uses). Many compounds can be classified as organic or inorganic by the presence or absence of certain typical properties, as illustrated in Table 1.1.1.

Key Takeaway

- Organic chemistry is the study of carbon compounds, nearly all of which also contain hydrogen atoms.

1.2: Drawing Chemical Structures

Objectives

After completing this section, you should be able to

1. propose one or more acceptable Kekulé structures (structural formulas) for any given molecular formula
2. write the molecular formula of a compound, given its Kekulé structure.
3. draw the shorthand structure of a compound, given its Kekulé structure.
4. interpret shorthand structures and convert them to Kekulé structures.
5. write the molecular formula of a compound, given its shorthand structure.

Study Notes

When drawing the structure of a neutral organic compound, you will find it helpful to remember that

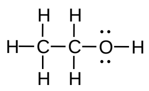
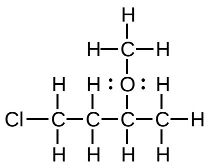
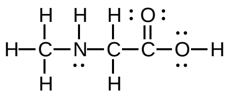
- each carbon atom has four bonds.
- each nitrogen atom has three bonds.
- each oxygen atom has two bonds.
- each hydrogen atom has one bond.

You may have already experienced looking at molecular structures using Lewis structures. Because organic chemistry can involve large molecules it would be beneficial if Lewis structures could be abbreviated. The three different ways to draw organic molecules include Kekulé Formulas, Condensed Formulas, and Skeletal structures (also called line-bond structures or line formulas). In this chapter, you will view molecules written in all three forms. It will be more helpful if you become comfortable going from one style of drawing to another, and look at drawings and understanding what they represent.

Simplification of structural formulas may be achieved without any loss of the information they convey. Kekule formulas is just organic chemistry's term for Lewis structures you have previously encountered. In **condensed structural formulas**, the bonds to each carbon are omitted, but each distinct structural unit (group) is written with subscript numbers designating multiple substituents, including the hydrogen atoms. **Line formulas** omit the symbols for carbon and hydrogen entirely (unless the hydrogen is bonded to an atom other than carbon). Each straight line segment represents a bond, the ends and intersections of the lines are carbon atoms, and the correct number of hydrogen atoms is calculated from the tetravalency of carbon. (Tetravalency refers to the tendency of carbon atoms to form 4 bonds.) Non-bonding valence shell electrons are omitted in these formulas.

Kekulé (a.k.a. Lewis Structures)

A Kekulé Formula or structural formula displays the atoms of the molecule in the order they are bonded. It also depicts how the atoms are bonded to one another, for example single, double, and triple covalent bond. Covalent bonds are shown using lines. The number of dashes indicate whether the bond is a single, double, or triple covalent bond. All atom labels are shown and all lone pairs are shown.

		
A	**B**	**C**

Condensed Formula

A condensed formula is made up of the elemental symbols. Condensed structural formulas show the order of atoms like a structural formula but are written in a single line to save space and make it more convenient and faster to write out. The order of the atoms suggests the connectivity in the molecule. Condensed structural formulas are also helpful when showing that a group of atoms is connected to a single atom in a compound. When this happens, parenthesis are used around the group of atoms to show they are together. Also, if more than one of the same substituent is attached to a given atom, it is show with a subscript number. An example is CH_4, which represents four hydrogen atoms attached to the same carbon. Condensed formulas can be read from either direction and H_3C is the same as CH_3, although the latter is more common.

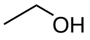
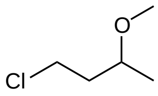
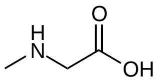
Look at the examples below and match them with their identical molecule under the Kekulé structures and the line formulas.

CH_3CH_2OH	$ClCH_2CH_2CH(OCH_3)CH_3$	CH_3NHCH_2COOH
A	**B**	**C**

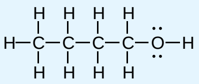
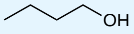
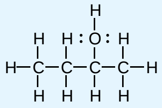
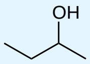
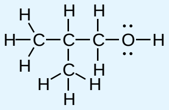
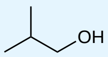
Let's look closely at example B. As you go through a condensed formula, you want to focus on the carbons and other elements that aren't hydrogen. The hydrogen's are important, but are usually there to complete octets. Also, notice the -OCH_3 is in written in parentheses which tell you that it not part of the main chain of carbons. As you read through a a condensed formula, if you reach an atom that doesn't have a complete octet by the time you reach the next hydrogen, then it's possible that there are double or triple bonds. In example C, the carbon is double bonded to oxygen and single bonded to another oxygen. Notice how COOH means C(=O)-O-H instead of CH_3-C-O-O-H because carbon does not have a complete octet if only one oxygen atom is bonded. The order in which the atoms are written in condensed structural formulas indicates a specific functional group (discussed later in this chapter).

Line Formula

Because organic compounds can be complex at times, line-angle formulas are used to write carbon and hydrogen atoms more efficiently by replacing the letter "C" with lines. A carbon atom is present wherever a line intersects another line. Hydrogen atoms are omitted but are assumed to be present to complete each of carbon's four bonds. Hydrogens that are attached to elements other than carbon are shown. Atom labels for all other elements are shown. Lone pair electrons are usually omitted. They are assumed to be present to complete the octet of non-carbon atoms. Line formulas help show the structure and order of the atoms in a compound.

		
A	**B**	**C**

These molecules correspond to the exact same molecules depicted for Kekulé structures and condensed formulas. Notice how the carbons are no longer drawn in and are replaced by the ends and bends of a lines. In addition, the hydrogen atoms have been omitted, but could be easily drawn in (see practice problems). Although we do not usually draw in the H's that are bonded to carbon, we do draw them in if they are connected to other atoms besides carbon (example is the OH group above in example A) . This is done because it is not always clear if the non-carbon atom is surrounded by lone pairs or hydrogen atoms. Also in example A, notice how the OH is drawn with a bond to the second carbon, but it does not mean that there is a third carbon at the end of that bond/ line.

Kekulé Formula	Condensed Formula	Line Formula
	$CH_3(CH_2)_3OH$	
	$CH_3CH_2CH(OH)CH_3$	
	$(CH_3)_2CHCH_2OH$	

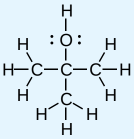
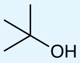
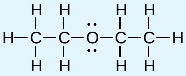
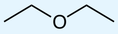
	$(CH_3)_3COH$	
	$CH_3CH_2OCH_2CH_3$	

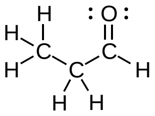
Table 1.2.1 : Structural Formulas for $C_4H_{10}O$ isomers

Example: Converting between Structural Formulas

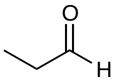
It is helpful to convert compounds into different structural formulas (Kekule, Line, and Condensed) depending on the type of question that is asked. Standardized exams frequently include a high percentage of condensed formulas because it is easier and cheaper to type letters and numbers than to import figures. Initially, it can be difficult writing a Line structure directly from a condensed formula. First, write the Kekule structure from the condensed formula and then draw the Line structure from the Kekule.

a) The condensed formula for propanal is CH_3CH_2CHO. Draw the Kekule structure.

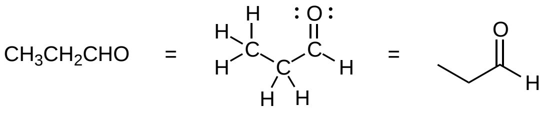
The Kekule structure for propanal is shown below. Remember that every carbon will have four bonds and oxygen atoms octet is filled with lone pairs.



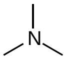
The bond-line structure for propanal is shown below. First, remove hydrogen atoms. The hydrogen attached to the aldehyde group remains because it is part of a functional group. The remove the "C" labels from the structure and keep the lines in place. Lastly, remove any lone pairs.



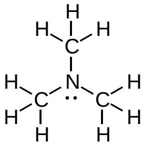
All three structures represent the same compound, propanal.



b) The following is the line structure of the molecule trimethyl amine.



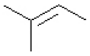
To convert it to a Kekule structure first identify the carbons in the molecule. The will be at the corners and ends of line without an atom label. Trimethyl amine has three carbons. Next, add hydrogen atoms to the carbons until four bonds are present. Each carbon in trimethyl amine is singly bonded to nitrogen. This means each carbon will need three additional C-H bonds to create its octet. Lastly, add lone pairs to other elements to fill their octets. The nitrogen in trimethyl amine is bonded to three carbons. This means it will require one of lone pair electrons to complete its octet.



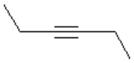
Exercises

1. How many carbons are in the following drawing? How many hydrogens?

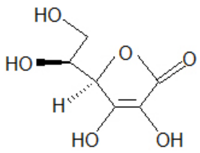
2. How many carbons are in the following drawing? How many hydrogens?



3. How many carbons are in the following drawing? How many hydrogens?



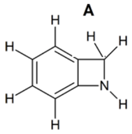
4. Look at the following molecule of vitamin C and draw in the hidden hydrogen atoms and electron pairs.



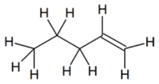
   (hint: Do all of the carbons have 4 bonds? Do all the oxygens have a full octet?)

5. Draw $ClCH_2CH_2CH(OCH_3)CH_3$ in Kekulé and line form.
6. Write down the molecular formula for each of the compounds shown here.

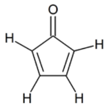
A



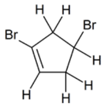
B



C

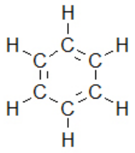


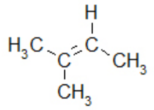
D



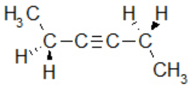
Answers:

1. Remember the octet rule and how many times carbons and hydrogenatoms are able to bond to other atoms.



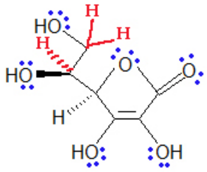


2.

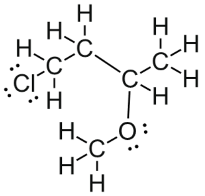


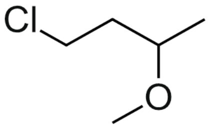
3.

4. Electron pairs drawn in blue and hydrogen atoms draw in red.



5.





6.

A. C_7H_7N
B. C_5H_{10}
C. C_5H_4O
D. $C_5H_6Br_2$

Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Dr. Krista Cunningham

1.3: Alkanes

Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.
- To give basic properties of alkanes.
- To name linear and branched alkanes using the IUPAC naming system.

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).

The three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are shown in Figure $1.3.1$.

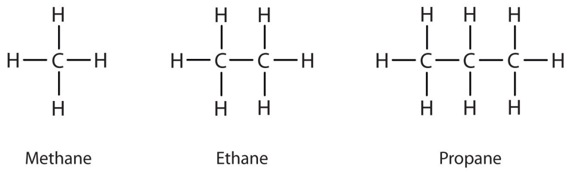


Figure $1.3.1$: The Three Simplest Alkanes

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 $1.3.2$).

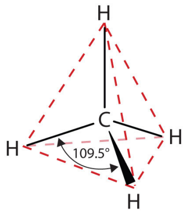


Figure $1.3.2$: The Tetrahedral Methane Molecule

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 $1.3.1$.

Table $1.3.1$: The First 10 Straight-Chain Alkanes

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

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

Consider the series in Figure 1.3.3. 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.

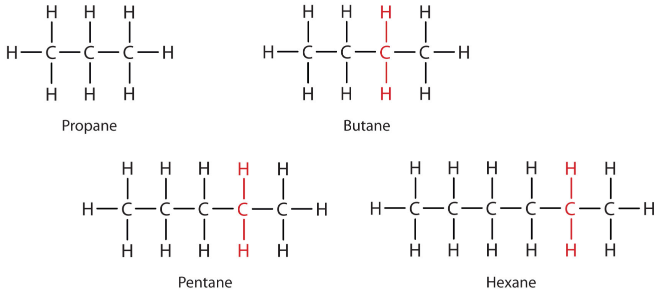


Figure 1.3.3: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

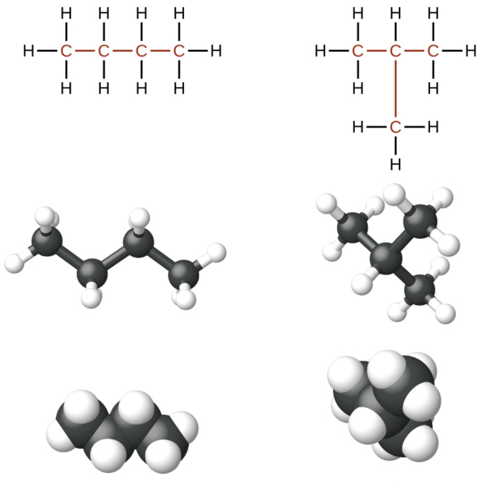
The principle of homology allows us to write a general formula for alkanes: C_nH_{2n+2}. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2 \times 8)+2} = C_8H_{18}$. The number of carbon atoms present in an alkane has no limit. Greater numbers of atoms in the molecules will lead to stronger intermolecular attractions (dispersion forces) and correspondingly different physical properties of the molecules. Properties such as melting point and boiling point (Table 1.3.2) usually change smoothly and predictably as the number of carbon and hydrogen atoms in the molecules change.

Table 1.3.2: Properties of Some Alkanes

Alkane	**Molecular Formula**	**Melting Point (°C)**	**Boiling Point (°C)**	**Phase at STP**[4]	**Number of Structural Isomers**
methane	CH_4	–182.5	–161.5	gas	1
ethane	C_2H_6	–183.3	–88.6	gas	1
propane	C_3H_8	–187.7	–42.1	gas	1
butane	C_4H_{10}	–138.3	–0.5	gas	2
pentane	C_5H_{12}	–129.7	36.1	liquid	3
hexane	C_6H_{14}	–95.3	68.7	liquid	5
heptane	C_7H_{16}	–90.6	98.4	liquid	9
octane	C_8H_{18}	–56.8	125.7	liquid	18
nonane	C_9H_{20}	–53.6	150.8	liquid	35
decane	$C_{10}H_{22}$	–29.7	174.0	liquid	75

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP[4]	Number of Structural Isomers
tetradecane	$C_{14}H_{30}$	5.9	253.5	solid	1858
octadecane	$C_{18}H_{38}$	28.2	316.1	solid	60,523

Hydrocarbons with the same formula, including alkanes, can have different structures. For example, two alkanes have the formula C_4H_{10}: They are called *n*-butane and 2-methylpropane (or isobutane), and have the following Lewis structures:



n-butane 2-methylpropane

The compounds *n*-butane and 2-methylpropane are structural isomers (the term constitutional isomers is also commonly used). Constitutional isomers have the same molecular formula but different spatial arrangements of the atoms in their molecules. The *n*-butane molecule contains an *unbranched chain*, meaning that no carbon atom is bonded to more than two other carbon atoms. We use the term *normal*, or the prefix *n*, to refer to a chain of carbon atoms without branching. The compound 2–methylpropane has a branched chain (the carbon atom in the center of the Lewis structure is bonded to three other carbon atoms).

Identifying isomers from Lewis structures is not as easy as it looks. Lewis structures that look different may actually represent the same isomers. For example, the three structures in Figure 1.3.4 all represent the same molecule, *n*-butane, and hence are not different isomers. They are identical because each contains an unbranched chain of four carbon atoms. We will discuss isomers in more detail later in this chapter.

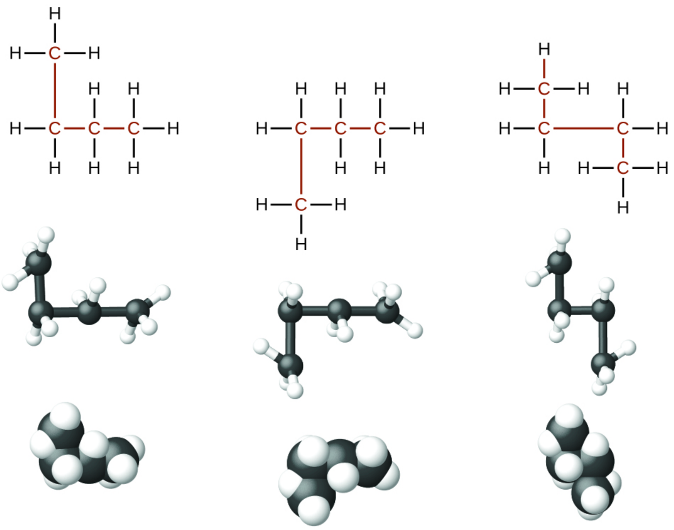
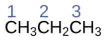


Figure 1.3.4: These three representations of the structure of n-butane are not isomers because they all contain the same arrangement of atoms and bonds.

The Basics of Organic Nomenclature: Naming Alkanes

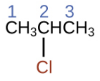
The International Union of Pure and Applied Chemistry (IUPAC) has devised a system of nomenclature that begins with the names of the alkanes and can be adjusted from there to account for more complicated structures. The nomenclature for alkanes is based on two rules:

1. To name an alkane, first identify the longest chain of carbon atoms in its structure. A two-carbon chain is called ethane; a three-carbon chain, propane; and a four-carbon chain, butane. Longer chains are named as follows: pentane (five-carbon chain), hexane (6), heptane (7), octane (8), nonane (9), and decane (10). These prefixes can be seen in the names of the alkanes described in Table $1.3.1$.
2. Add prefixes to the name of the longest chain to indicate the positions and names of substituents. Substituents are branches or functional groups that replace hydrogen atoms on a chain. The position of a substituent or branch is identified by the number of the carbon atom it is bonded to in the chain. We number the carbon atoms in the chain by counting from the end of the chain nearest the substituents. Multiple substituents are named individually and placed in alphabetical order at the front of the name.
3.



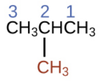
$CH_3CH_2CH_3$

propane



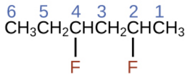
CH_3CHCH_3 with Cl on C2

2-chloropropane



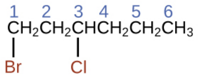
CH_3CHCH_3 with CH_3 on C2

2-methylpropane



$CH_3CH_2CHCH_2CHCH_3$ with F on C4 and C2

2,4-difluorohexane



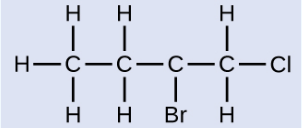
$CH_2CH_2CHCH_2CH_2CH_3$ with Br on C1 and Cl on C3

1-bromo-3-chlorohexane

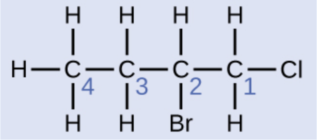
When more than one substituent is present, either on the same carbon atom or on different carbon atoms, the substituents are listed alphabetically. Because the carbon atom numbering begins at the end closest to a substituent, the longest chain of carbon atoms is numbered in such a way as to produce the lowest number for the substituents. The ending *-o* replaces *-ide* at the end of the name of an electronegative substituent (in ionic compounds, the negatively charged ion ends with *-ide* like chloride; in organic compounds, such atoms are treated as substituents and the *-o* ending is used). The number of substituents of the same type is indicated by the prefixes *di-* (two), *tri-* (three), *tetra-* (four), and so on (for example, *difluoro-* indicates two fluoride substituents).

✓ Example 1.3.1: Naming Halogen-substituted Alkanes

Name the molecule whose structure is shown here:



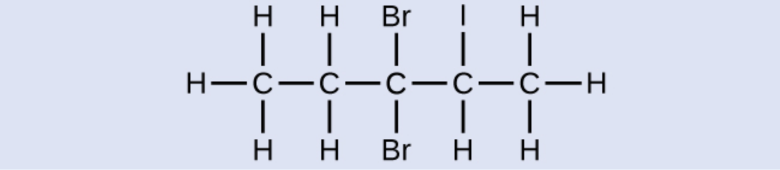
Solution



The four-carbon chain is numbered from the end with the chlorine atom. This puts the substituents on positions 1 and 2 (numbering from the other end would put the substituents on positions 3 and 4). Four carbon atoms means that the base name of this compound will be butane. The bromine at position 2 will be described by adding 2-bromo-; this will come at the beginning of the name, since bromo- comes before chloro- alphabetically. The chlorine at position 1 will be described by adding 1-chloro-, resulting in the name of the molecule being 2-bromo-1-chlorobutane.

? Exercise 1.3.1

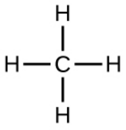
Name the following molecule:



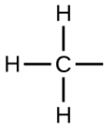
Answer

3,3-dibromo-2-iodopentane

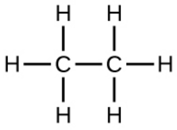
We call a substituent that contains one less hydrogen than the corresponding alkane an alkyl group. The name of an alkyl group is obtained by dropping the suffix *-ane* of the alkane name and adding *-yl*:



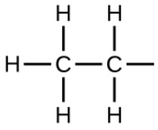
methane



methyl group



ethane

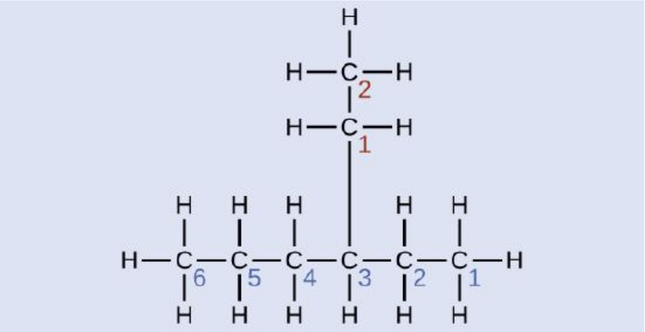


ethyl group

The open bonds in the methyl and ethyl groups indicate that these alkyl groups are bonded to another atom.

✓ Example 1.3.2 Naming Substituted Alkanes

Name the molecule whose structure is shown here:

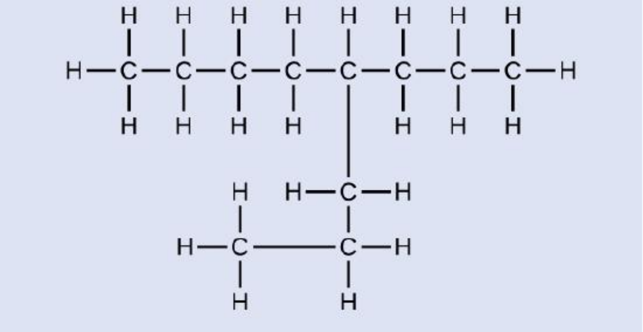


Solution

The longest carbon chain runs horizontally across the page and contains six carbon atoms (this makes the base of the name hexane, but we will also need to incorporate the name of the branch). In this case, we want to number from right to left (as shown by the blue numbers) so the branch is connected to carbon 3 (imagine the numbers from left to right—this would put the branch on carbon 4, violating our rules). The branch attached to position 3 of our chain contains two carbon atoms (numbered in red)—so we take our name for two carbons *eth-* and attach *-yl* at the end to signify we are describing a branch. Putting all the pieces together, this molecule is 3-ethylhexane.

? Exercise 1.3.2

Name the following molecule:



Answer

4-propyloctane

Some hydrocarbons can form more than one type of alkyl group when the hydrogen atoms that would be removed have different “environments” in the molecule. This diversity of possible alkyl groups can be identified in the following way: The four hydrogen atoms in a methane molecule are equivalent; they all have the same environment. They are equivalent because each is bonded to a carbon atom (the same carbon atom) that is bonded to three hydrogen atoms. (It may be easier to see the equivalency in the ball and stick models in Figure 1.3.4. Removal of any one of the four hydrogen atoms from methane forms a methyl group. Likewise, the six hydrogen atoms in ethane are equivalent and removing any one of these hydrogen atoms produces an ethyl group. Each of the six hydrogen atoms is bonded to a carbon atom that is bonded to two other hydrogen atoms and a carbon atom. However, in both propane and 2–methylpropane, there are hydrogen atoms in two different environments, distinguished by the adjacent atoms or groups of atoms:

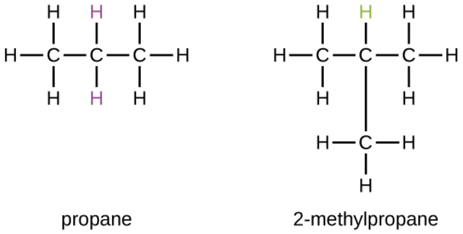
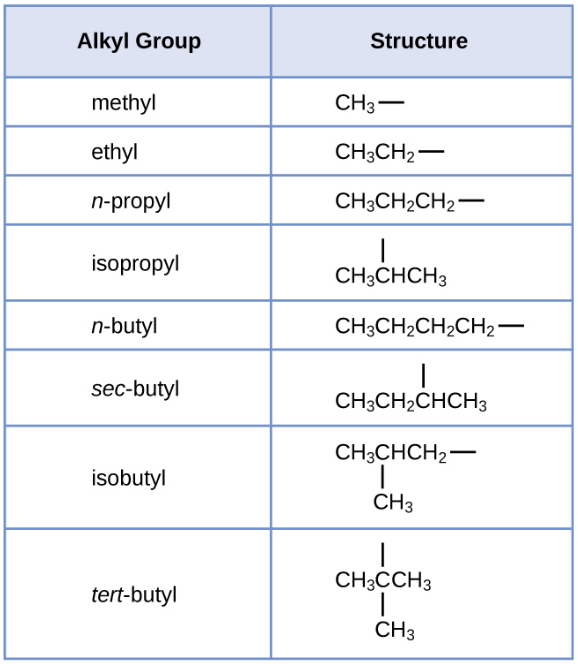


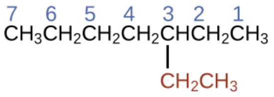
Figure 1.3.5.



Alkyl Group	Structure
methyl	$CH_3—$
ethyl	$CH_3CH_2—$
n-propyl	$CH_3CH_2CH_2—$
isopropyl	$CH_3\overset{\vert}{C}HCH_3$
n-butyl	$CH_3CH_2CH_2CH_2—$
sec-butyl	$CH_3CH_2\overset{\vert}{C}HCH_3$
isobutyl	$CH_3\underset{\underset{\displaystyle CH_3}{\vert}}{C}HCH_2—$
tert-butyl	$CH_3\overset{\vert}{\underset{\underset{\displaystyle CH_3}{\vert}}{C}}CH_3$

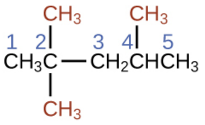
Figure 1.3.6: This listing gives the names and formulas for various alkyl groups formed by the removal of hydrogen atoms from different locations.

Note that alkyl groups do not exist as stable independent entities. They are always a part of some larger molecule. The location of an alkyl group on a hydrocarbon chain is indicated in the same way as any other substituent:



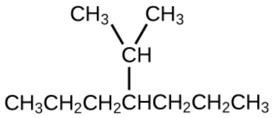
$$\overset{7}{C}H_3\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}H_2\underset{\underset{\displaystyle CH_2CH_3}{\vert}}{\overset{3}{C}}H\overset{2}{C}H_2\overset{1}{C}H_3$$

3-ethylheptane



$$\overset{1}{C}H_3\overset{\overset{\displaystyle CH_3}{\vert}}{\underset{\underset{\displaystyle CH_3}{\vert}}{\overset{2}{C}}}—\overset{3}{C}H_2\overset{\overset{\displaystyle CH_3}{\vert}}{\overset{4}{C}}H\overset{5}{C}H_3$$

2,2,4-trimethylpentane



$$CH_3CH_2CH_2\overset{\overset{\displaystyle (CH_3)_2CH}{\vert}}{C}HCH_2CH_2CH_3$$

4-isopropylheptane

Alkanes are relatively stable molecules, but heat or light will activate reactions that involve the breaking of C–H or C–C single bonds. Combustion is one such reaction:

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) \tag{1.3.1}$$

Alkanes burn in the presence of oxygen, a highly exothermic oxidation-reduction reaction that produces carbon dioxide and water. As a consequence, alkanes are excellent fuels. For example, methane, CH_4, is the principal component of natural gas. Butane, C_4H_{10}, used in camping stoves and lighters is an alkane. Gasoline is a liquid mixture of continuous- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel. Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses. The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation. Fractional distillation takes advantage of differences in the boiling points of the components of the mixture (Figure 1.3.7). You may recall that boiling point is a function of intermolecular interactions, which was discussed in the chapter on solutions and colloids.

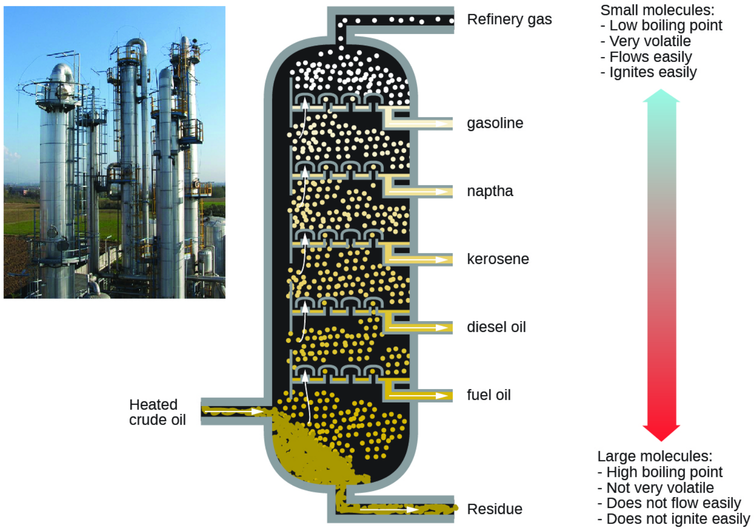


Figure 1.3.7:In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. (credit left: modification of work by Luigi Chiesa)

Key Takeaways

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.
- Alkanes have low boiling points, are flammable, and are not soluble in water.
- The IUPAC naming system can distinguish between different isomers for a family of alkanes.

1.4: Unsaturated Hydrocarbons

Learning Objectives

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

Alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C=CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds ($R–C≡C–R$). In these condensed structural formulas "R" is an abbreviation for the rest of the molecule. R-groups are often used in organic chemistry when one distinct part of a molecule is being discussed.

Collectively, alkenes and alkynes 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:

Alkenes

Organic compounds that contain one or more double or triple bonds between carbon atoms are described as unsaturated. You have likely heard of unsaturated fats. These are complex organic molecules with long chains of carbon atoms, which contain at least one double bond between carbon atoms. Unsaturated hydrocarbon molecules that contain one or more double bonds are called alkenes. Carbon atoms linked by a double bond are bound together by two bonds, one σ bond and one π bond. Double and triple bonds give rise to a different geometry around the carbon atom that participates in them, leading to important differences in molecular shape and properties. The differing geometries are responsible for the different properties of unsaturated versus saturated fats.

Ethene, C_2H_4, is the simplest alkene. Each carbon atom in ethene, commonly called ethylene, has a trigonal planar structure. The second member of the series is propene (propylene) (Figure 1.4.1); the butene isomers follow in the series. Four carbon atoms in the chain of butene allows for the formation of isomers based on the position of the double bond, as well as a new form of isomerism.

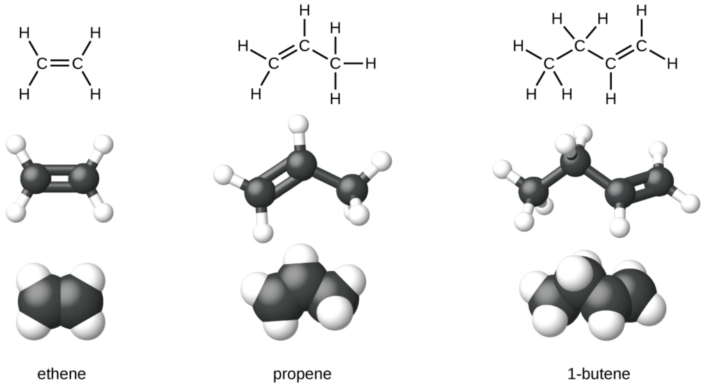


Figure 1.4.1: Expanded structures, ball-and-stick structures, and space-filling models for the alkenes ethene, propene, and 1-butene are shown.

Some representative alkenes—their names, structures, and physical properties—are given in Table 1.4.1.

Table 1.4.1: Physical Properties of Some Selected Alkenes

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)

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

The first two alkenes in Table 1.4.1, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure 1.4.2). 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.

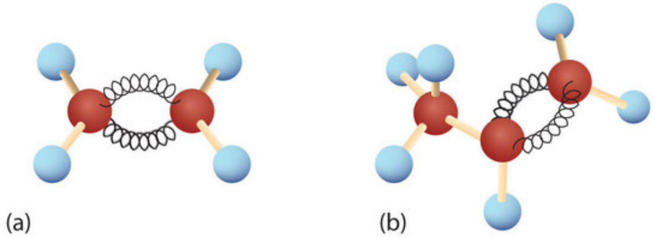
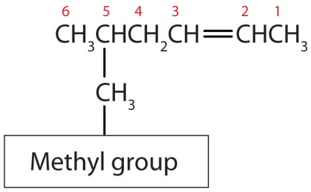


Figure 1.4.2: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

> 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):

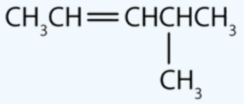
1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound $CH_2{=}CHCH_3$ is *propene*.
2. If there are four or 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.*

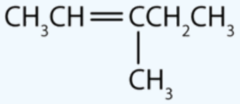


$$\overset{6}{C}H_3\underset{\displaystyle CH_3}{\overset{5}{C}H}\overset{4}{C}H_2\overset{3}{C}H{=}\overset{2}{C}H\overset{1}{C}H_3$$

Example 1.4.1

Name each compound.

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

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

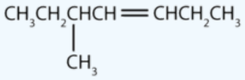
Solution

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 1.4.1

Name each compound.

1. $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$
2. 
$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH{=}CHCH_2CH_3$

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.

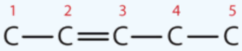
Example 1.4.2

Draw the structure for each compound.

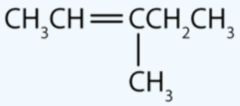
1. 3-methyl-2-pentene
2. cyclohexene

Solution

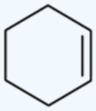
1. First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:


$\overset{1}{C}-\overset{2}{C}{=}\overset{3}{C}-\overset{4}{C}-\overset{5}{C}$

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.


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

2. 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 1.4.2

Draw the structure for each compound.

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

Alkynes

Hydrocarbon molecules with one or more triple bonds are called alkynes; they make up another series of unsaturated hydrocarbons. Two carbon atoms joined by a triple bond are bound together by one σ bond and two π bonds. The *sp*-hybridized carbons involved in the triple bond have bond angles of 180°, giving these types of bonds a linear, rod-like shape.

The simplest member of the alkyne series is ethyne, C_2H_2, commonly called acetylene. The Lewis structure for ethyne, a linear molecule, is:

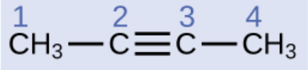

$H-C\equiv C-H$

ethyne (acetylene)

The IUPAC nomenclature for alkynes is similar to that for alkenes except that the suffix *-yne* is used to indicate a triple bond in the chain. For example, $\mathrm{CH_3CH_2C\equiv CH}$ is called 1-butyne.

Example 1.4.3: Structure of Alkynes

Describe the geometry and hybridization of the carbon atoms in the following molecule:

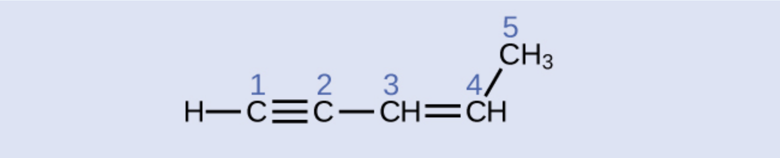

$\overset{1}{CH_3}-\overset{2}{C}\equiv\overset{3}{C}-\overset{4}{CH_3}$

Solution

Carbon atoms 1 and 4 have four single bonds and are thus tetrahedral with sp^3 hybridization. Carbon atoms 2 and 3 are involved in the triple bond, so they have linear geometries and would be classified as *sp* hybrids.

Exercise 1.4.3

Identify the hybridization and bond angles at the carbon atoms in the molecule shown:



Answer

carbon 1: *sp*, 180°; carbon 2: *sp*, 180°; carbon 3: sp^2, 120°; carbon 4: sp^2, 120°; carbon 5: sp^3, 109.5°

Aromatic Hydrocarbons

Benzene, C_6H_6, is the simplest member of a large family of hydrocarbons, called aromatic hydrocarbons. These compounds contain ring structures and exhibit bonding that must be described using the resonance hybrid concept of valence bond theory or the delocalization concept of molecular orbital theory. (To review these concepts, refer to the earlier chapters on chemical bonding). The resonance structures for benzene, C_6H_6, are:

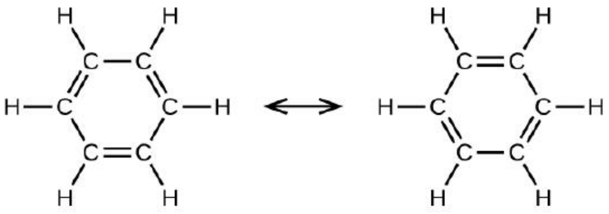


Figure 1.4.3.

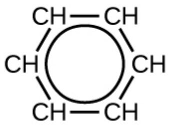
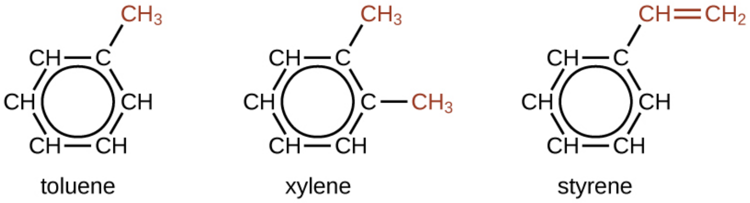


Figure 1.4.3: This condensed formula shows the unique bonding structure of benzene.

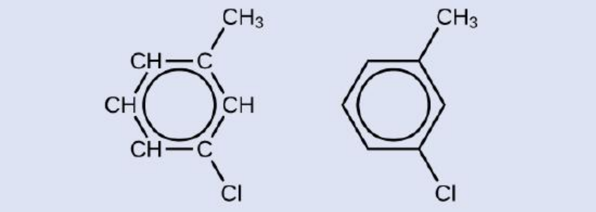
There are many derivatives of benzene. The hydrogen atoms can be replaced by many different substituents. Aromatic compounds more readily undergo substitution reactions than addition reactions; replacement of one of the hydrogen atoms with another substituent will leave the delocalized double bonds intact. The following are typical examples of substituted benzene derivatives:



Toluene and xylene are important solvents and raw materials in the chemical industry. Styrene is used to produce the polymer polystyrene.

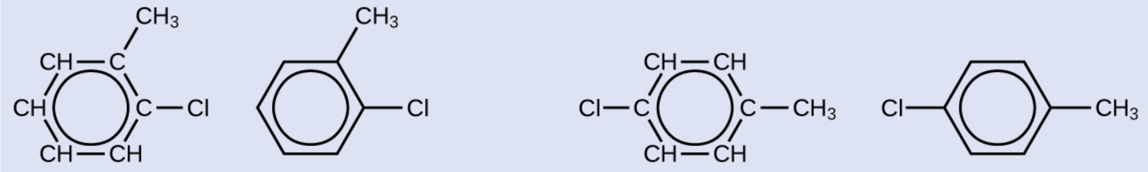
✓ Example 1.4.4: Structure of Aromatic Hydrocarbons

One possible isomer created by a substitution reaction that replaces a hydrogen atom attached to the aromatic ring of toluene with a chlorine atom is shown here. Draw two other possible isomers in which the chlorine atom replaces a different hydrogen atom attached to the aromatic ring:



Solution

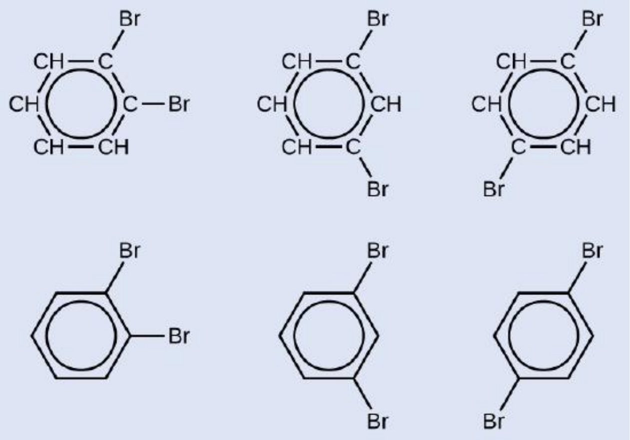
Since the six-carbon ring with alternating double bonds is necessary for the molecule to be classified as aromatic, appropriate isomers can be produced only by changing the positions of the chloro-substituent relative to the methyl-substituent:



Exercise 1.4.4

Draw three isomers of a six-membered aromatic ring compound substituted with two bromines.

Answer



Contributors and Attributions

Key Takeaways

- Alkenes are hydrocarbons with one or more carbon-to-carbon double bonds.
- Alkynes are hydrocarbons with one or more carbon-to-carbon triple bonds.
- Aromatic hydrocarbons contain ring structures with delocalized π electron systems.

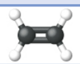
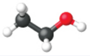
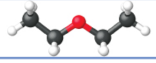
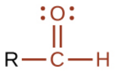
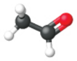
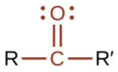
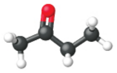
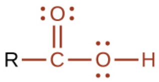
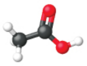
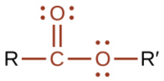
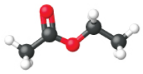
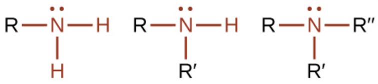
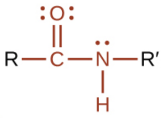
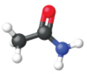
1.5: Organic Compounds with Functional Groups

Learning Objectives

- to describe functional groups and explain why they are useful in the study of organic chemistry.
- to identify and name common functional groups.

Previously, we considered several kinds of hydrocarbons, compounds that consist of only carbon and hydrogen. Many organic compounds contain additional elements present as part of functional groups. A functional group is a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to the molecule. If you understand the behavior of a particular functional group, you will know a great deal about the general properties of that class of compounds. Some common functional groups are listed in Table 1.5.1. Each family is based on a common, simple functional group that contains an oxygen atom, a sulfur atom, or a nitrogen atom.

Table 1.5.1: Selected Organic Functional Groups

Compound Name	**Structure of Compound and Functional Group (red)**	**Example**			
		Formula		**Name**
alkene	$C{=}C$	C_2H_4 	ethene
alkyne	$C{\equiv}C$	C_2H_2 	ethyne
alcohol	$R{-}\ddot{\underset{\cdot\cdot}{O}}{-}H$	CH_3CH_2OH 	ethanol
ether	$R{-}\ddot{\underset{\cdot\cdot}{O}}{-}R'$	$(C_2H_5)_2O$ 	diethyl ether
aldehyde	 $R{-}\overset{\overset{:\ddot{O}:}{\|}}{C}{-}H$	CH_3CHO 	ethanal
ketone	 $R{-}\overset{\overset{:\ddot{O}:}{\|}}{C}{-}R'$	$CH_3COCH_2CH_3$ 	methyl ethyl ketone
carboxylic acid	 $R{-}\overset{\overset{:\ddot{O}:}{\|}}{C}{-}\ddot{\underset{\cdot\cdot}{O}}{-}H$	CH_3COOH 	acetic acid
ester	 $R{-}\overset{\overset{:\ddot{O}:}{\|}}{C}{-}\ddot{\underset{\cdot\cdot}{O}}{-}R'$	$CH_3CO_2CH_2CH_3$ 	ethyl acetate
amine	 $R{-}\underset{\underset{H}{\|}}{\ddot{N}}{-}H$ $R{-}\underset{\underset{R'}{\|}}{\ddot{N}}{-}H$ $R{-}\underset{\underset{R'}{\|}}{\ddot{N}}{-}R''$	$C_2H_5NH_2$ 	ethylamine
amide	 $R{-}\overset{\overset{:\ddot{O}:}{\|}}{C}{-}\underset{\underset{H}{\|}}{\ddot{N}}{-}R'$	CH_3CONH_2 	acetamide

Although this table considered each functional group separately, these groups can be present in the same molecule. The structure and the reactivity of each molecule depends on its size and its presence of functional groups.

> Organic molecules can be very large, often molecules contain more that one functional group.

Consider the amino acid serine, shown in Figure 1.5.1. Three functional groups are present in the molecule: an amine, an alcohol, and a carboxylic acid.

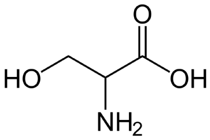


Figure 1.5.1. Line formula for the amino acid serine.

Key Takeaways

- The functional group, a structural arrangement of atoms and/or bonds, is largely responsible for the properties of organic compound families.
- Compounds can contain one or more functional group.

Concept Review Exercises

1. What is the functional group of an alkene? An alkyne?
2. Does $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ have a functional group? Explain.

Answers

1. carbon-to-carbon double bond; carbon-to-carbon triple bond
2. No; it has nothing but carbon and hydrogen atoms and all single bonds.

1.6: Structural Isomerism in Organic Molecules

What is structural isomerism?

Organic compounds with the same formula can have different structures. For example, two alkanes have the formula C_4H_{10}: They are called *n*-butane and 2-methylpropane (or isobutane), and have the following Lewis structures:

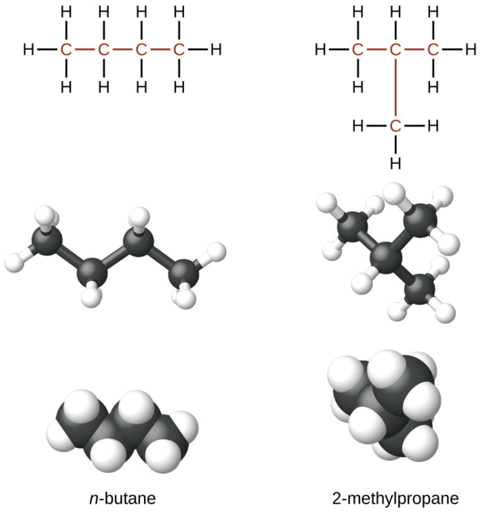


Figure 1.6.1: Structural isomers of C_4H_{10}

The compounds *n*-butane and 2-methylpropane are structural isomers (the term constitutional isomers is also commonly used). **Constitutional isomers** have the same molecular formula but different spatial arrangements of the atoms in their molecules. The *n*-butane molecule contains an *unbranched chain*, meaning that no carbon atom is bonded to more than two other carbon atoms. We use the term *normal*, or the prefix *n*, to refer to a chain of carbon atoms without branching. The compound 2–methylpropane has a branched chain (the carbon atom in the center of the Lewis structure is bonded to three other carbon atoms)

Identifying isomers from Lewis structures is not as easy as it looks. Lewis structures that look different may actually represent the same isomers. For example, the three structures in Figure 1.6.2 all represent the same molecule, *n*-butane, and hence are not different isomers. They are identical because each contains an unbranched chain of four carbon atoms.

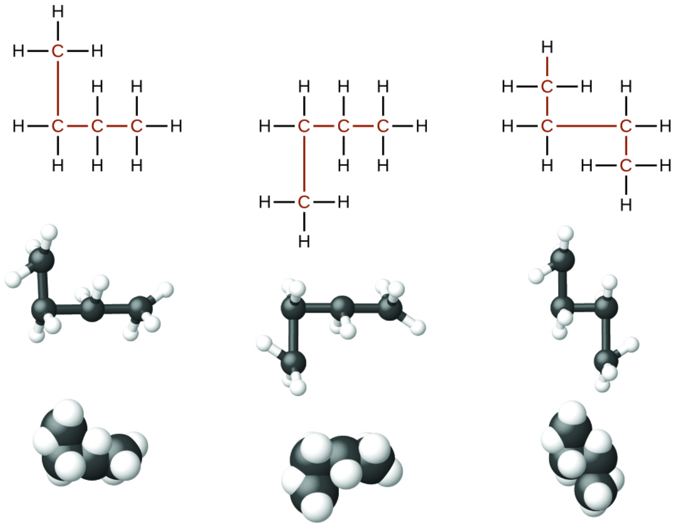


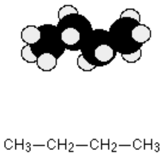
Figure 1.6.2: These three representations of the structure of n-butane are not isomers because they all contain the same arrangement of atoms and bonds.

There are also endless other possible ways that this molecule could twist itself. There is completely free rotation around all the carbon-carbon single bonds. If you had a model of a molecule in front of you, you would have to take it to pieces and rebuild it if you wanted to make an isomer of that molecule. If you can make an apparently different molecule just by rotating single bonds, it's not different - it's still the same molecule.

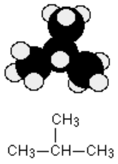
In structural isomerism, the atoms are bonded in a different arrangement. This is easier to see with specific examples. What follows looks at some of the ways that structural isomers can arise.

Chain Isomerism

These isomers arise because of the possibility of branching in carbon chains. For example, there are two isomers of butane, C_4H_{10}. In one of them, the carbon atoms lie in a "straight chain" whereas in the other the chain is branched.



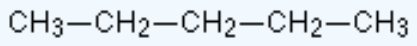
$CH_3{-}CH_2{-}CH_2{-}CH_3$



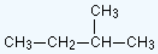
$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}CH_3$

Example 1.6.1: Chain Isomers in Pentane

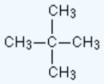
Pentane, C_5H_{12}, has three chain isomers. If you think you can find any others, they are simply twisted versions of the ones below. If in doubt make some models.



$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3$



$CH_3{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}CH_3$



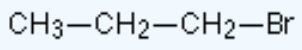
$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}CH_3$

Position isomerism

In position isomerism, the basic carbon skeleton remains unchanged, but important groups are moved around on that skeleton.

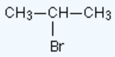
Example 1.6.2: Positional Isomers in C_5H_{12}

For example, there are two structural isomers with the molecular formula C_3H_7Br. In one of them the bromine atom is on the end of the chain, whereas in the other it's attached in the middle.



$CH_3{-}CH_2{-}CH_2{-}Br$

1-bromopropane

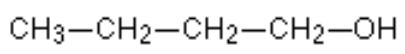


$CH_3{-}\underset{\displaystyle Br}{\underset{|}{C}H}{-}CH_3$

2-bromopropane

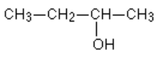
If you made a model, there is no way that you could twist one molecule to turn it into the other one. You would have to break the bromine off the end and re-attach it in the middle. At the same time, you would have to move a hydrogen from the middle to the end.

Another similar example occurs in alcohols such as C_4H_9OH



$CH_3{-}CH_2{-}CH_2{-}CH_2{-}OH$

butan-1-ol

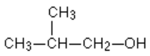


$CH_3{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{C}H}{-}CH_3$

butan-2-ol

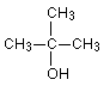
These are the only two possibilities provided you keep to a four carbon chain, but there is no reason why you should do that. You can easily have a mixture of chain isomerism and position isomerism - you aren't restricted to one or the other.

So two other isomers of butanol are:



$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}CH_2{-}OH$

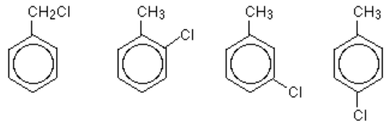
2-methylpropan-1-ol



$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}{-}CH_3$

2-methylpropan-2-ol

You can also get position isomers on rings. Consider the molecular formula C_7H_7Cl. There are four different isomers you could make depending on the position of the chlorine atom. In one case it is attached to the side-group carbon atom, and then there are three other possible positions it could have around the ring - next to the CH_3 group, next-but-one to the CH_3 group, or opposite the CH_3 group.

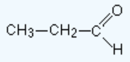


Functional group isomerism

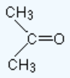
In this variety of structural isomerism, the isomers contain different functional groups - that is, they belong to different families of compounds (different homologous series).

Example 1.6.3: Isomers in C_3H_6O

A molecular formula C_3H_6O could be either propanal (an aldehyde) or propanone (a ketone).



propanal

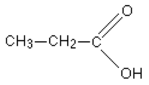


propanone

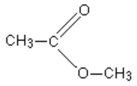
There are other possibilities as well for this same molecular formula - for example, you could have a carbon-carbon double bond (an alkene) and an -OH group (an alcohol) in the same molecule.

$$CH_2{=}CH{-}CH_2{-}OH$$

Another common example is illustrated by the molecular formula $C_3H_6O_2$. Amongst the several structural isomers of this are propanoic acid (a carboxylic acid) and methyl ethanoate (an ester).



propanoic acid



methyl ethanoate

Contributors

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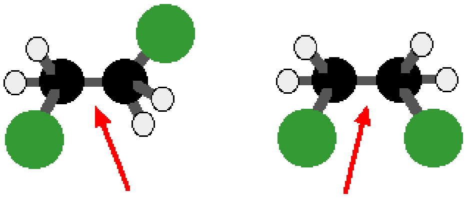
1.7: Stereoisomerism in Organic Molecules

What are stereoisomers?

Isomers are molecules that have the same molecular formula, but have a different arrangement of the atoms in space. That excludes any different arrangements which are simply due to the molecule rotating as a whole, or rotating about particular bonds. Where the atoms making up the various isomers are joined up in a different order, this is known as structural isomerism. Structural isomerism is **not** a form of stereoisomerism, which involve the atoms of the complex bonded in the same order, but in different spatial arrangements. Geometric isomerism is one form of stereoisomerism; optical isomerism is a second type.

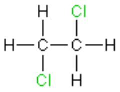
Geometric (cis / trans) isomerism

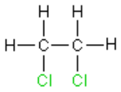
Geometric isomerism (also known as cis-trans isomerism or E-Z isomerism) is a form of stereoisomerism. These isomers occur where you have restricted rotation somewhere in a molecule. At an introductory level in organic chemistry, examples usually just involve the carbon-carbon double bond - and that's what this page will concentrate on. Think about what happens in molecules where there is unrestricted rotation about carbon bonds - in other words where the carbon-carbon bonds are all single. The next diagram shows two possible configurations of 1,2-dichloroethane.



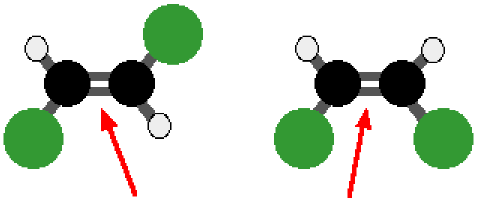
free rotation about this single bond

These two images represent exactly the same molecule. You can get from one to the other just by twisting around the carbon-carbon single bond. These molecules are not isomers. If you draw a structural formula instead of using models, you have to bear in mind the possibility of this free rotation about single bonds. You must accept that these two structures represent the same molecule:





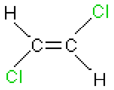
But what happens if you have a carbon-carbon double bond - as in 1,2-dichloroethene?



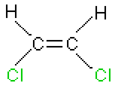
no rotation about this double bond

These two molecules are not the same. The carbon-carbon double bond won't rotate and so you would have to take the models to pieces in order to convert one structure into the other one. That is a simple test for isomers. If you have to take a model to pieces to convert it into another one, then you've got isomers. If you merely have to twist it a bit, then you haven't!

Drawing structural formulae for the last pair of models gives two possible isomers. In one, the two chlorine atoms are locked on opposite sides of the double bond. This is known as the ***trans*** isomer. (*trans*: from latin meaning "across" - as in transatlantic). In the other, the two chlorine atoms are locked on the same side of the double bond. This is know as the ***cis*** isomer. (*cis*: from latin meaning "on this side").



trans-1,2-dichloroethene

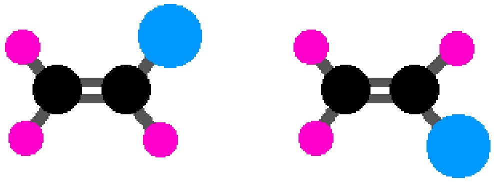


cis-1,2-dichloroethene

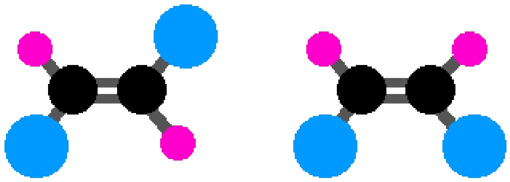
How to recognize the possibility of geometric isomerism

Geometric isomerism requires restricted rotation somewhere in the molecule. The two most common structures that generate geometric isomers are 1) a carbon-carbon double bond, and 2) a ring. However, having a carbon-carbon double bond or a ring in a molecule does not guarantee that there will be geometric isomerism.

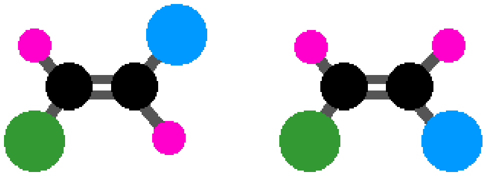
Think about this case:



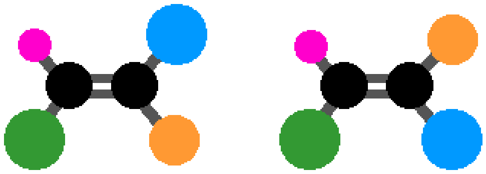
What needs to be attached to the carbon-carbon double bond? Although we've swapped the right-hand groups around, these are still the same molecule. To get from one to the other, all you would have to do is to turn the whole model over. You won't have geometric isomers if there are two groups the same on one end of the bond - in this case, the two pink groups on the left-hand end. So there must be two different groups on the left-hand carbon and two different groups on the right-hand one. The cases we've been exploring earlier are like this:



But you could make things even more different and still have geometric isomers:



Here, the blue and green groups are either on the same side of the bond or the opposite side. Or you could go the whole hog and make everything different. You still get geometric isomers, but by now the words cis and trans are meaningless. This is where the more sophisticated E-Z notation comes in.



Now let's consider a compound containing a ring.

Optical isomerism

Optical isomers are named like this because of their effect on plane polarized light. Simple substances which show optical isomerism exist as two isomers known as **enantiomers**.

- A solution of one enantiomer rotates the plane of polarization in a clockwise direction. This enantiomer is known as the (+) form.
- For example, one of the optical isomers (enantiomers) of the amino acid alanine is known as (+)alanine.
- A solution of the other enantiomer rotates the plane of polarization in an anti-clockwise direction. This enantiomer is known as the (-) form. So the other enantiomer of alanine is known as or (-)alanine.
- If the solutions are equally concentrated the amount of rotation caused by the two isomers is exactly the same - but in opposite directions.

- When optically active substances are made in the lab, they often occur as a 50/50 mixture of the two enantiomers. This is known as a racemic mixture or racemate. It has no effect on plane polarized light.

Origin of Optical Isomers

The examples of organic optical isomers contain a carbon atom joined to **four** different groups. These two models each have the same groups joined to the central carbon atom, but still manage to be different:

Obviously as they are drawn, the orange and blue groups are not aligned the same way. Could you get them to align by rotating one of the molecules? The next diagram shows what happens if you rotate molecule B.

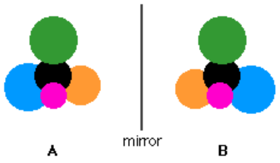
They still are not the same - and there is no way that you can rotate them so that they look exactly the same. These are isomers of each other. They are described as being non-superimposable in the sense that (if you imagine molecule B being turned into a ghostly version of itself) you couldn't slide one molecule exactly over the other one. Something would always be pointing in the wrong direction.

What happens if two of the groups attached to the central carbon atom are the same? The next diagram shows this possibility.

The two models are aligned exactly as before, but the orange group has been replaced by another pink one. Rotating molecule **B** this time shows that it is exactly the same as molecule A. You only get optical isomers if all four groups attached to the central carbon are different.

The relationship between the enantiomers

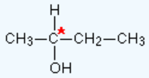
One of the enantiomers is simply a non-superimposable mirror image of the other one. In other words, if one isomer looked in a mirror, what it would see is the other one. The two isomers (the original one and its mirror image) have a different spatial arrangement, and so cannot be superimposed on each other.



If an achiral molecule (one with a plane of symmetry) looked in a mirror, you would always find that by rotating the image in space, you could make the two look identical. It would be possible to superimpose the original molecule and its mirror image.

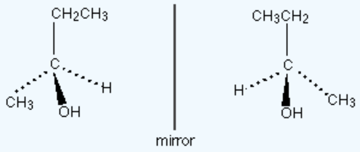
Example 1: Isobutanol

The asymmetric carbon atom in a compound (the one with four different groups attached) is often shown by a star.



$$CH_3-\overset{H}{\underset{OH}{\overset{*}{C}}}-CH_2-CH_3$$

It's extremely important to draw the isomers correctly. Draw one of them using standard bond notation to show the 3-dimensional arrangement around the asymmetric carbon atom. Then draw the mirror to show the examiner that you know what you are doing, and then the mirror image.

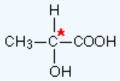


Notice that you don't literally draw the mirror images of all the letters and numbers! It is, however, quite useful to reverse large groups - look, for example, at the ethyl group at the top of the diagram. It doesn't matter in the least in what order you draw the four groups around the central carbon. As long as your mirror image is drawn accurately, you will automatically have drawn the two isomers.

So which of these two isomers is (+)butan-2-ol and which is (-)butan-2-ol? There is no simple way of telling that. For A'level purposes, you can just ignore that problem - all you need to be able to do is to draw the two isomers correctly.

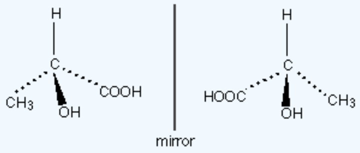
Example 2: 2-hydroxypropanoic acid (lactic acid)

Once again the chiral center is shown by a star.

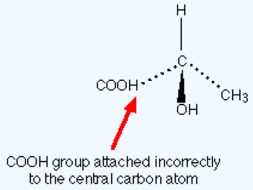


$$CH_3-\overset{H}{\underset{OH}{\overset{*}{C}}}-COOH$$

The two enantiomers are:



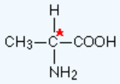
It is important this time to draw the COOH group backwards in the mirror image. If you don't there is a good chance of you joining it on to the central carbon wrongly.



If you draw it like this in an exam, you will not get the mark for that isomer even if you have drawn everything else perfectly.

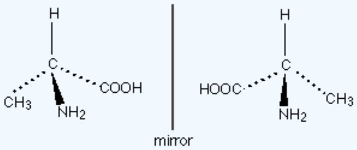
Example 3: 2-aminopropanoic acid (alanine)

This is typical of naturally-occurring amino acids. Structurally, it is just like the last example, except that the -OH group is replaced by $-NH_2$



$$CH_3-\overset{H}{\underset{NH_2}{\overset{*}{C}}}-COOH$$

The two enantiomers are:



Only one of these isomers occurs naturally: the (+) form. You cannot tell just by looking at the structures which this is.

It has, however, been possible to work out which of these structures is which. Naturally occurring alanine is the right-hand structure, and the way the groups are arranged around the central carbon atom is known as an **L-** configuration. Notice the use of the capital L. The other configuration is known as **D-**.

So you may well find alanine described as L-(+)alanine. That means that it has this particular structure and rotates the plane of polarization clockwise.

Even if you know that a different compound has an arrangement of groups similar to alanine, you still cannot say which way it will rotate the plane of polarization. The other amino acids, for example, have the same arrangement of groups as alanine does (all that changes is the CH_3 group), but some are (+) forms and others are (-) forms.

It's quite common for natural systems to only work with one of the enantiomers of an optically active substance. It is not too difficult to see why that might be. Because the molecules have different spatial arrangements of their various groups, only one of them is likely to fit properly into the active sites on the enzymes they work with.

In the lab, it is quite common to produce equal amounts of both forms of a compound when it is synthesized. This happens just by chance, and you tend to get racemic mixtures.

Chiral and achiral molecules

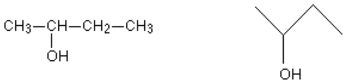
The essential difference between the two examples we've looked at lies in the symmetry of the molecules. If there are two groups the same attached to the central carbon atom, the molecule has a plane of symmetry. If you imagine slicing through the molecule, the left-hand side is an exact reflection of the right-hand side.

Where there are four groups attached, there is no symmetry anywhere in the molecule

A molecule which has no plane of symmetry is described as chiral. The carbon atom with the four different groups attached which causes this lack of symmetry is described as a chiral center or as an asymmetric carbon atom. The molecule on the left above (with a plane of symmetry) is described as achiral. Only chiral molecules have optical isomers.

Identifying Chiral Centers

A skeletal formula is the most stripped-down formula possible. Look at the structural formula and skeletal formula for butan-2-ol.



Notice that in the skeletal formula all of the carbon atoms have been left out, as well as all of the hydrogen atoms attached to carbons. In a skeletal diagram of this sort:

- there is a carbon atom at each junction between bonds in a chain and at the end of each bond (unless there is something else there already - like the -OH group in the example);
- there are enough hydrogen atoms attached to each carbon to make the total number of bonds on that carbon up to 4.

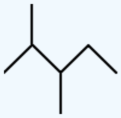
We have already discussed the butan-2-ol case further up the page, and you know that it has optical isomers. The second carbon atom (the one with the -OH attached) has four different groups around it, and so is a chiral center.

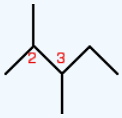
Is this obvious from the skeletal formula? Well, it is, provided you remember that each carbon atom has to have 4 bonds going away from it. Since the second carbon here only seems to have 3, there must also be a hydrogen attached to that carbon. So it has a hydrogen, an -OH group, and two different hydrocarbon groups (methyl and ethyl).

Four different groups around a carbon atom means that it is a chiral center.

✓ Example 4: A slightly more complicated case: 2,3-dimethylpentane

The diagrams show an uncluttered skeletal formula, and a repeat of it with two of the carbons labeled.



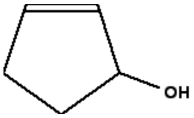


Look first at the carbon atom labeled 2. Is this a chiral center? No, it is not. Two bonds (one vertical and one to the left) are both attached to methyl groups. In addition, of course, there is a hydrogen atom and the more complicated hydrocarbon group to the right. It doesn't have 4 different groups attached, and so is not a chiral center.

What about the number 3 carbon atom? This has a methyl group below it, an ethyl group to the right, and a more complicated hydrocarbon group to the left. Plus, of course, a hydrogen atom to make up the 4 bonds that have to be formed by the carbon. That means that it is attached to 4 different things, and so is a chiral center.

Introducing Rings

We will start with a fairly simple ring compound:

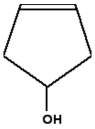


When you are looking at rings like this, as far as optical isomerism is concerned, you don't need to look at any carbon in a double bond. You also don't need to look at any junction which only has two bonds going away from it. In that case, there must be 2 hydrogens attached, and so there cannot possibly be 4 different groups attached.

In this case, that means that you only need to look at the carbon with the -OH group attached. It has an -OH group, a hydrogen (to make up the total number of bonds to four), and links to two carbon atoms. How does the fact that these carbon atoms are part of a ring affect things?

You just need to trace back around the ring from both sides of the carbon you are looking at. Is the arrangement in both directions exactly the same? In this case, it is not. Going in one direction, you come immediately to a carbon with a double bond. In the other direction, you meet two singly bonded carbon atoms, and then one with a double bond. That means that you haven't got two identical hydrocarbon groups attached to the carbon you are interested in, and so it has 4 different groups in total around it. It is asymmetric - a chiral center.

What about this near-relative of the last molecule?



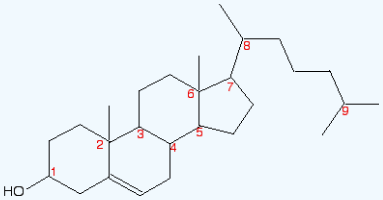
In this case, everything is as before, except that if you trace around the ring clockwise and counter-clockwise from the carbon at the bottom of the ring, there is an identical pattern in both directions. You can think of the bottom carbon being attached to a hydrogen, an -OH group, and two identical hydrocarbon groups. It therefore is **not** a chiral center.

The other thing which is very noticeable about this molecule is that there is a plane of symmetry through the carbon atom we are interested in. If you chopped it in half through this carbon, one side of the molecule would be an exact reflection of the other. In the first ring molecule above, that is not the case.

If you can see a plane of symmetry through the carbon atom it will not be a chiral center. If there is not a plane of symmetry, it will be a chiral center.

Example 5: Cholesterol

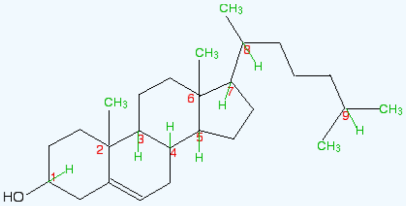
The skeletal diagram shows the structure of cholesterol. Some of the carbon atoms have been numbered for discussion purposes below. These are **not** part of the normal system for numbering the carbon atoms in cholesterol.



Before you read on, look carefully at each of the numbered carbon atoms, and decide which of them are chiral centers. The other carbon atoms in the structure cannot be chiral centers, because they are either parts of double bonds, or are joined to either two or three hydrogen atoms.

So . . . how many chiral centers did you find? In fact, there are 8 chiral centers out of the total of 9 carbons marked. If you didn't find all eight, go back and have another look before you read any further. It might help to sketch the structure on a piece of paper and draw in any missing hydrogens attached to the numbered carbons, and write in the methyl groups at the end of the branches as well.

This is done for you below, but it would be a lot better if you did it yourself and then checked your sketch afterwards .



Starting with the easy one - it is obvious that carbon 9 has two methyl groups attached. It doesn't have 4 different groups, and so cannot be chiral. If you take a general look at the rest, it is fairly clear that none of them has a plane of symmetry through the numbered carbons. Therefore they are all likely to be chiral centers. But it's worth checking to see what is attached to each of them.

- Carbon 1 has a hydrogen, an -OH and two different hydrocarbon chains (actually bits of rings) attached. Check clockwise and anticlockwise, and you will see that the arrangement is not identical in each direction. Four different groups means a chiral center.
- Carbon 2 has a methyl and three other different hydrocarbon groups. If you check along all three bits of rings , they are all different - another chiral center. This is also true of carbon 6.
- Carbons 3, 4, 5 and 7 are all basically the same. Each is attached to a hydrogen and three different bits of rings. All of these are chiral centers.
- Finally, carbon 8 has a hydrogen, a methyl group, and two different hydrocarbon groups attached. Again, this is a chiral center.

This all looks difficult at first glance, but it is not. You do, however, have to take a great deal of care in working through it - it is amazingly easy to miss one out.

Summary

To get geometric isomers you must have:

- restricted rotation (often involving a carbon-carbon double bond or a ring for introductory purposes);
- two different groups on the left-hand end of the bond and two different groups on the right-hand end. It doesn't matter whether the left-hand groups are the same as the right-hand ones or not.

Contributors

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1.8: Optical Isomerism in Organic Molecules

Optical isomerism is a form of stereoisomerism. This page explains what stereoisomers are and how you recognize the possibility of optical isomers in a molecule.

What are stereoisomers?

Isomers are molecules that have the same molecular formula, but have a different arrangement of the atoms in space. That excludes any different arrangements which are simply due to the molecule rotating as a whole, or rotating about particular bonds. Where the atoms making up the various isomers are joined up in a different order, this is known as structural isomerism. Structural isomerism is **not** a form of stereoisomerism, which involve the atoms of the complex bonded in the same order, but in different spatial arrangements. Optical isomerism is one form of stereoisomerism; geometric isomers are a second type.

Optical isomerism

Optical isomers are named like this because of their effect on plane polarized light. Simple substances which show optical isomerism exist as two isomers known as enantiomers.

- A solution of one enantiomer rotates the plane of polarisation in a clockwise direction. This enantiomer is known as the (+) form.
- For example, one of the optical isomers (enantiomers) of the amino acid alanine is known as (+)alanine.
- A solution of the other enantiomer rotates the plane of polarisation in an anti-clockwise direction. This enantiomer is known as the (-) form. So the other enantiomer of alanine is known as or (-)alanine.
- If the solutions are equally concentrated the amount of rotation caused by the two isomers is exactly the same - but in opposite directions.
- When optically active substances are made in the lab, they often occur as a 50/50 mixture of the two enantiomers. This is known as a racemic mixture or racemate. It has no effect on plane polarised light.

Origin of Optical Isomers

The examples of organic optical isomers contain a carbon atom joined to **four** different groups. These two models each have the same groups joined to the central carbon atom, but still manage to be different:

Obviously as they are drawn, the orange and blue groups are not aligned the same way. Could you get them to align by rotating one of the molecules? The next diagram shows what happens if you rotate molecule B.

They still are not the same - and there is no way that you can rotate them so that they look exactly the same. These are isomers of each other. They are described as being non-superimposable in the sense that (if you imagine molecule B being turned into a ghostly version of itself) you couldn't slide one molecule exactly over the other one. Something would always be pointing in the wrong direction.

What happens if two of the groups attached to the central carbon atom are the same? The next diagram shows this possibility.

The two models are aligned exactly as before, but the orange group has been replaced by another pink one. Rotating molecule **B** this time shows that it is exactly the same as molecule A. You only get optical isomers if all four groups attached to the central carbon are different.

Chiral and achiral molecules

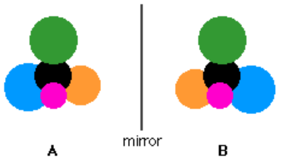
The essential difference between the two examples we've looked at lies in the symmetry of the molecules. If there are two groups the same attached to the central carbon atom, the molecule has a plane of symmetry. If you imagine slicing through the molecule, the left-hand side is an exact reflection of the right-hand side.

Where there are four groups attached, there is no symmetry anywhere in the molecule

A molecule which has no plane of symmetry is described as chiral. The carbon atom with the four different groups attached which causes this lack of symmetry is described as a chiral center or as an asymmetric carbon atom. The molecule on the left above (with a plane of symmetry) is described as achiral. Only chiral molecules have optical isomers.

The relationship between the enantiomers

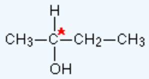
One of the enantiomers is simply a non-superimposable mirror image of the other one. In other words, if one isomer looked in a mirror, what it would see is the other one. The two isomers (the original one and its mirror image) have a different spatial arrangement, and so cannot be superimposed on each other.



If an achiral molecule (one with a plane of symmetry) looked in a mirror, you would always find that by rotating the image in space, you could make the two look identical. It would be possible to superimpose the original molecule and its mirror image.

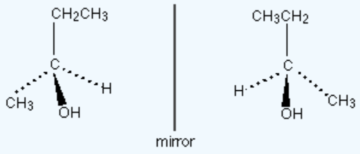
Example 1: Isobutanol

The asymmetric carbon atom in a compound (the one with four different groups attached) is often shown by a star.



$CH_3-\overset{H}{\underset{OH}{C^*}}-CH_2-CH_3$

It's extremely important to draw the isomers correctly. Draw one of them using standard bond notation to show the 3-dimensional arrangement around the asymmetric carbon atom. Then draw the mirror to show the examiner that you know what you are doing, and then the mirror image.

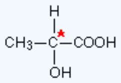


Notice that you don't literally draw the mirror images of all the letters and numbers! It is, however, quite useful to reverse large groups - look, for example, at the ethyl group at the top of the diagram. It doesn't matter in the least in what order you draw the four groups around the central carbon. As long as your mirror image is drawn accurately, you will automatically have drawn the two isomers.

So which of these two isomers is (+)butan-2-ol and which is (-)butan-2-ol? There is no simple way of telling that. For A'level purposes, you can just ignore that problem - all you need to be able to do is to draw the two isomers correctly.

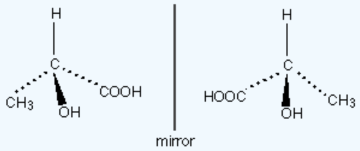
✓ Example 2: 2-hydroxypropanoic acid (lactic acid)

Once again the chiral center is shown by a star.

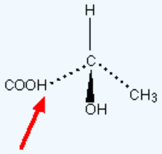


$CH_3-C^*H(OH)-COOH$

The two enantiomers are:



It is important this time to draw the COOH group backwards in the mirror image. If you don't there is a good chance of you joining it on to the central carbon wrongly.

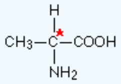


COOH group attached incorrectly
to the central carbon atom

If you draw it like this in an exam, you will not get the mark for that isomer even if you have drawn everything else perfectly.

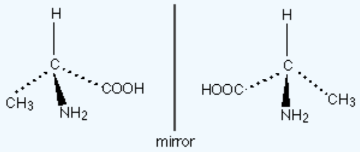
✓ Example 3: 2-aminopropanoic acid (alanine)

This is typical of naturally-occurring amino acids. Structurally, it is just like the last example, except that the -OH group is replaced by $-NH_2$



$CH_3-C^*H(NH_2)-COOH$

The two enantiomers are:



Only one of these isomers occurs naturally: the (+) form. You cannot tell just by looking at the structures which this is.

It has, however, been possible to work out which of these structures is which. Naturally occurring alanine is the right-hand structure, and the way the groups are arranged around the central carbon atom is known as an **L-** configuration. Notice the use of the capital L. The other configuration is known as **D-**.

So you may well find alanine described as L-(+)alanine. That means that it has this particular structure and rotates the plane of polarization clockwise.

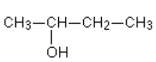
Even if you know that a different compound has an arrangement of groups similar to alanine, you still cannot say which way it will rotate the plane of polarization. The other amino acids, for example, have the same arrangement of groups as alanine does (all that changes is the CH_3 group), but some are (+) forms and others are (-) forms.

It's quite common for natural systems to only work with one of the enantiomers of an optically active substance. It is not too difficult to see why that might be. Because the molecules have different spatial arrangements of their various groups, only one of them is likely to fit properly into the active sites on the enzymes they work with.

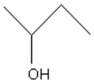
In the lab, it is quite common to produce equal amounts of both forms of a compound when it is synthesized. This happens just by chance, and you tend to get racemic mixtures.

Identifying Chiral Centers

A skeletal formula is the most stripped-down formula possible. Look at the structural formula and skeletal formula for butan-2-ol.



$CH_3-\underset{OH}{CH}-CH_2-CH_3$



Notice that in the skeletal formula all of the carbon atoms have been left out, as well as all of the hydrogen atoms attached to carbons. In a skeletal diagram of this sort:

- there is a carbon atom at each junction between bonds in a chain and at the end of each bond (unless there is something else there already - like the -OH group in the example);
- there are enough hydrogen atoms attached to each carbon to make the total number of bonds on that carbon up to 4.

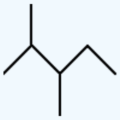
We have already discussed the butan-2-ol case further up the page, and you know that it has optical isomers. The second carbon atom (the one with the -OH attached) has four different groups around it, and so is a chiral center.

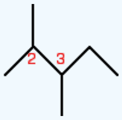
Is this obvious from the skeletal formula? Well, it is, provided you remember that each carbon atom has to have 4 bonds going away from it. Since the second carbon here only seems to have 3, there must also be a hydrogen attached to that carbon. So it has a hydrogen, an -OH group, and two different hydrocarbon groups (methyl and ethyl).

Four different groups around a carbon atom means that it is a chiral center.

✓ Example 4: A slightly more complicated case: 2,3-dimethylpentane

The diagrams show an uncluttered skeletal formula, and a repeat of it with two of the carbons labeled.



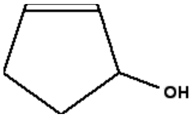


Look first at the carbon atom labeled 2. Is this a chiral center? No, it is not. Two bonds (one vertical and one to the left) are both attached to methyl groups. In addition, of course, there is a hydrogen atom and the more complicated hydrocarbon group to the right. It doesn't have 4 different groups attached, and so is not a chiral center.

What about the number 3 carbon atom? This has a methyl group below it, an ethyl group to the right, and a more complicated hydrocarbon group to the left. Plus, of course, a hydrogen atom to make up the 4 bonds that have to be formed by the carbon. That means that it is attached to 4 different things, and so is a chiral center.

Introducing Rings

We will start with a fairly simple ring compound:

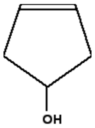


When you are looking at rings like this, as far as optical isomerism is concerned, you don't need to look at any carbon in a double bond. You also don't need to look at any junction which only has two bonds going away from it. In that case, there must be 2 hydrogens attached, and so there cannot possibly be 4 different groups attached.

In this case, that means that you only need to look at the carbon with the -OH group attached. It has an -OH group, a hydrogen (to make up the total number of bonds to four), and links to two carbon atoms. How does the fact that these carbon atoms are part of a ring affect things?

You just need to trace back around the ring from both sides of the carbon you are looking at. Is the arrangement in both directions exactly the same? In this case, it is not. Going in one direction, you come immediately to a carbon with a double bond. In the other direction, you meet two singly bonded carbon atoms, and then one with a double bond. That means that you haven't got two identical hydrocarbon groups attached to the carbon you are interested in, and so it has 4 different groups in total around it. It is asymmetric - a chiral center.

What about this near-relative of the last molecule?



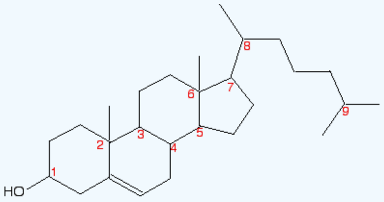
In this case, everything is as before, except that if you trace around the ring clockwise and counter-clockwise from the carbon at the bottom of the ring, there is an identical pattern in both directions. You can think of the bottom carbon being attached to a hydrogen, an -OH group, and two identical hydrocarbon groups. It therefore is **not** a chiral center.

The other thing which is very noticeable about this molecule is that there is a plane of symmetry through the carbon atom we are interested in. If you chopped it in half through this carbon, one side of the molecule would be an exact reflection of the other. In the first ring molecule above, that is not the case.

If you can see a plane of symmetry through the carbon atom it will not be a chiral center. If there is not a plane of symmetry, it will be a chiral center.

✓ Example 5: Cholesterol

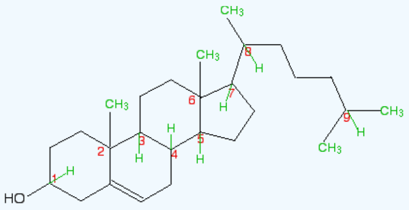
The skeletal diagram shows the structure of cholesterol. Some of the carbon atoms have been numbered for discussion purposes below. These are **not** part of the normal system for numbering the carbon atoms in cholesterol.



Before you read on, look carefully at each of the numbered carbon atoms, and decide which of them are chiral centers. The other carbon atoms in the structure cannot be chiral centers, because they are either parts of double bonds, or are joined to either two or three hydrogen atoms.

So . . . how many chiral centers did you find? In fact, there are 8 chiral centers out of the total of 9 carbons marked. If you didn't find all eight, go back and have another look before you read any further. It might help to sketch the structure on a piece of paper and draw in any missing hydrogens attached to the numbered carbons, and write in the methyl groups at the end of the branches as well.

This is done for you below, but it would be a lot better if you did it yourself and then checked your sketch afterwards .



Starting with the easy one - it is obvious that carbon 9 has two methyl groups attached. It doesn't have 4 different groups, and so cannot be chiral. If you take a general look at the rest, it is fairly clear that none of them has a plane of symmetry through the numbered carbons. Therefore they are all likely to be chiral centers. But it's worth checking to see what is attached to each of them.

- Carbon 1 has a hydrogen, an -OH and two different hydrocarbon chains (actually bits of rings) attached. Check clockwise and anticlockwise, and you will see that the arrangement is not identical in each direction. Four different groups means a chiral center.
- Carbon 2 has a methyl and three other different hydrocarbon groups. If you check along all three bits of rings , they are all different - another chiral center. This is also true of carbon 6.
- Carbons 3, 4, 5 and 7 are all basically the same. Each is attached to a hydrogen and three different bits of rings. All of these are chiral centers.
- Finally, carbon 8 has a hydrogen, a methyl group, and two different hydrocarbon groups attached. Again, this is a chiral center.

This all looks difficult at first glance, but it is not. You do, however, have to take a great deal of care in working through it - it is amazingly easy to miss one out.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

1.9: Organic Reactions

Learning Outcomes

- Identify and describe substitution, elimination, addition, hydrolysis, and condensation reactions.
- Explain why some condensation reactions are also called dehydration reactions.
- Define "polymer".

Organic reactions require the breaking of strong covalent bonds, which takes a considerable input of energy. In order for relatively stable organic molecules to react at a reasonable rate, they often must be modified with the use of highly reactive materials or in the presence of a catalyst. In this lesson, you will learn about several general categories of organic reactions.

Substitution Reactions

A **substitution reaction**, which is the same as a single replacement reaction in inorganic reactions, *is a reaction in which one or more atoms in a molecule are replaced with another atom or group of atoms.* Alkyl halides are formed by the substitution of a halogen atom for a hydrogen atom. When methane reacts with chlorine gas, ultraviolet light can act as a catalyst for the reaction.

$$\mathrm{CH_4}\,(g) + \mathrm{Cl_2}\,(g) \overset{\text{UV light}}{\rightarrow} \mathrm{CH_3Cl}\,(g) + \mathrm{HCl}\,(g) \tag{1.9.1}$$

The reaction produces chloromethane and hydrogen chloride. When the mixture is allowed to react for longer periods of time, further substitution reactions may occur.

$$\mathrm{CH_3Cl}\,(g) + \mathrm{Cl_2}\,(g) \overset{\text{UV light}}{\rightarrow} \mathrm{CH_2Cl_2}\,(g) + \mathrm{HCl}\,(g) \tag{1.9.2}$$

The product above is dichloromethane. Further substitution products trichloromethane and tetrachloromethane, commonly called carbon tetrachloride. A mixture of products occurs in the reaction, with the relative amounts dependent upon the time that the reaction is allowed to proceed. Chlorofluorocarbons are produced by reacting chloroalkanes with HF, because the fluorine atom makes a stronger bond to the carbon atom than chlorine does.

$$\mathrm{CCl_4}\,(g) + \mathrm{HF}\,(g) \overset{\mathrm{SbF_5}}{\rightarrow} \mathrm{CCl_3F}\,(g) + \mathrm{HCl}\,(g) \tag{1.9.3}$$

The fluorine atom substitutes for a chlorine atom in the reaction.

Elimination Reactions

An **elimination reaction** involves the removal of adjacent atoms from a molecule. This results in the formation of a multiple bond and the release of a small molecule, so they are called elimination reactions. A typical example is the conversion of ethyl chloride to ethylene:

$$CH_3CH_2Cl \rightarrow CH_2 = CH_2 + HCl \tag{1.9.4}$$

Much of the approximately 26 million tons of ethene (i.e. ethylene) produced per year in the United States is used to synthesize plastics, such as polyethylene. In the above reaction, the molecule eliminated is HCl, whose components are eliminated as H^+ from the carbon atom on the left and Cl^- from the carbon on the right. When an acid is produced, as occurs here, the reaction is generally carried out in the presence of a base (such as NaOH) to neutralize the acid. Other elimination reactions will produce H_2, X_2 (where X = halogen), or H_2O. These reactions are often referred to by more descriptive terms such as dehydrogenation (removing hydrogen) or dechlorination (removing chlorine).

Addition Reactions

An **addition reaction** *is a reaction in which an atom or molecule is added to an unsaturated molecule, making a single product.* An addition reaction can often be thought of as adding a molecule across the double bond of an alkene or across the triple bond of an alkyne. Knowing that "ation" means to add, the specific names of these reactions, such as hydrogenation, hydration, or chlorination, should make sense. Note that hydrogenation (adding H_2) and hydration (adding H_2O) are very different processes.

One type of addition reaction is called hydrogenation. **Hydrogenation** *is a reaction that occurs when molecular hydrogen is added to an alkene to produce an alkane* or *hydrogen is added to an alkyne to produce an alkene or alkane.* The reaction is typically performed with the use of a transition metal catalyst. For example, ethene reacts with hydrogen to form ethane.

$$\mathrm{CH_2{=}CH_2}\,(g) + \mathrm{H_2}\,(g) \xrightarrow{\mathrm{Pt}} \mathrm{CH_3CH_3}\,(g) \tag{1.9.5}$$

Note that the hydrogenation reaction is also a redox reaction. Ethene is reduced, because the oxidation numbers of the carbon atoms change from -2 to -3 as a result of the reaction.

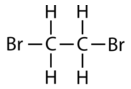
Vegetable oils consist of long carbon chains with carboxyl groups on the end; these molecules are referred to as fatty acids. The carbon chains of the fatty acids in vegetable oils are unsaturated, usually containing multiple double bonds. When hydrogen gas is blown through a sample of the oil, hydrogen atoms add across the double bonds. This conversion changes the substance from a liquid oil into a solid fat. The "hydrogenated" on a food product is an indication that oil (liquid) has been converted into fat (solid) by this process. Margarine is manufactured from unsaturated vegetable oil in this way by hydrogenating some of the double bonds making it a "partially hydrogenated vegetable oil".

Addition reactions are also useful ways to introduce a new functional group into an organic molecule. Alkyl halides can be produced from an alkene by the addition of either the elemental halogen or the hydrogen halide. A monosubstituted alkyl halide can be produced by the addition of a hydrogen halide to an alkene. Shown below is the formation of chloroethane.

$$\mathrm{CH_2{=}CH_2}\,(g) + \mathrm{HCl}\,(g) \rightarrow \mathrm{CH_3CH_2Cl}\,(g) \tag{1.9.6}$$

When the reactant is the diatomic halogen, the product is a disubstituted alkyl halide as in the addition of bromine to ethene.

$$\mathrm{CH_2{=}CH_2}\,(g) + \mathrm{Br_2}\,(l) \rightarrow \mathrm{CH_2BrCH_2Br}\,(g) \tag{1.9.7}$$



1,2-dibromoethane

The addition of bromine to an unknown organic compound can be used as a test for unsaturation in the compound. Bromine has a distinctive brownish-orange color, while most bromoalkanes are colorless. When bromine is slowly added to a solution of the compound, the orange color will fade if it undergoes an addition reaction to produce an alkyl halide. If the orange color remains, then the original compound was already saturated, and no reaction occurred.

A **hydration reaction** *is a reaction in which water is added to an alkene*. Hydration reactions can take place when the alkene and water are heated to near $100^{\mathrm{o}}\mathrm{C}$ in the presence of a strong acid, which acts as a catalyst. Shown below is the hydration of ethene to produce ethanol.

$$\mathrm{CH_2{=}CH_2}\,(g) + \mathrm{H_2O}\,(l) \rightarrow \mathrm{CH_3CH_2OH}\,(g) \tag{1.9.8}$$

Condensation Reactions

A **condensation reaction** *is a reaction in which two molecules combine to form a single molecule.* A small molecule, often water, is usually removed during a condensation reaction. Amino acids are important biological molecules that have an amine functional group on one end of the molecule and a carboxylic acid functional group on the other end. When two amino acids combine in a condensation reaction, a covalent bond forms between the amine nitrogen of one amino acid and the carboxyl carbon of the second amino acid. A molecule of water is then removed as a second product (see figure below).

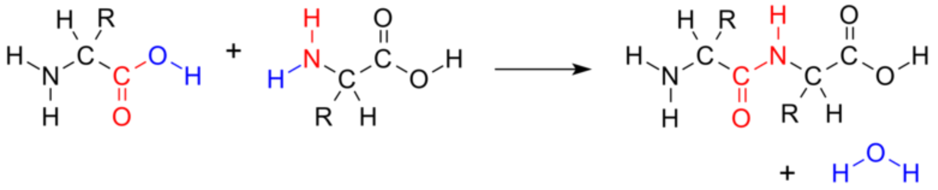
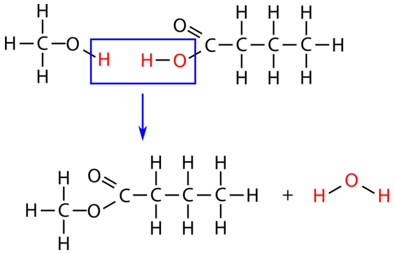


Figure 1.9.1: Amino acids join together to form a molecule called a dipeptide. The $-\mathrm{OH}$ from the carboxyl group of one amino acid combines with a hydrogen atom from the amine group of the other amino group to produce water (blue).

This reaction forms a molecule called a dipeptide, and the resulting carbon-nitrogen covalent bond is often called a peptide bond. When repeated numerous times, a long molecule called a protein is eventually produced.

An **esterification** *is a* condensation *reaction in which an ester is formed from an alcohol and a carboxylic acid.* Esterification is a subcategory of condensation reactions because a water molecule is produced in the reaction. The reaction can be catalyzed by a strong acid, usually sulfuric acid. When the carboxylic acid, butanoic acid, is heated with an excess of methanol and a few drops of sulfuric acid, the ester methyl butanoate is produced. Methyl butanoate has the scent of pineapples. The reaction is shown below with both molecular and structural formulas. Esterification reactions are reversible.

$$CH_3CH_2CH_2COOH + HOCH_3 \overset{H_2SO_4}{\rightarrow} CH_3CH_2CH_2COOCH_3 + H_2O \tag{1.9.9}$$



Polymerization

Polymerization occurs when several condensation reactions or addition reactions occur in sequence to result in a large organic molecule. Polymers are very different than the other kinds of organic molecules that you have seen so far. Whereas other compounds are of relatively low molar mass, polymers are giant molecules of very high molar mass. Polymers are the primary components of all sorts of plastics and related compounds. A **polymer** *is a large molecule formed of many smaller molecules covalently bonded to one another in a repeating pattern*. The *small molecules that make up the polymer are called* **monomers**. Teflon (see figure below) is a non-reactive, non-stick coating used on cookware as well as in containers and pipes for reactive or corrosive chemicals.

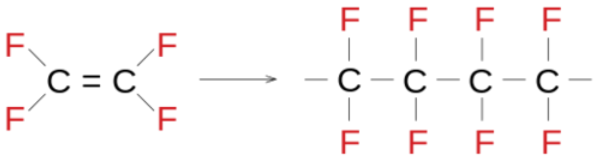


Figure 1.9.2: Polytetrafluoroethylene (also known as Teflon) is formed from the polymerization of tetrafluoroethylene.

Hydrolysis Reactions

Hydrolysis is the reverse of condensation. "Hydro" indicates that water is involved and "lysis" means to break apart. In a hydrolysis reaction, water is added and the molecule breaks apart, usually at a $C-O-C$ linkage.

Saponification *describes the alkaline hydrolysis reaction of an ester*. The term saponification originally described the hydrolysis of long-chain esters called fatty acids esters to produce soap molecules, which are the salts of fatty acids. One such soap molecule is sodium stearate, formed from the hydrolysis of ethyl stearate.

$$\underset{\text{ethyl stearate}}{C_{17}H_{35}COOC_2H_5} + NaOH \rightarrow \underset{\text{sodium stearate (soap)}}{C_{17}H_{35}COO{-}Na^+} + C_2H_5OH \tag{1.9.10}$$

Contributors and Attributions

-
- Allison Soult, Ph.D. (Department of Chemistry, University of Kentucky)

1.10: Organic Chemistry (Exercises)

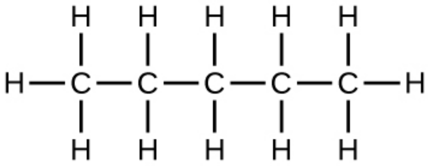
1. Write the chemical formula and Lewis structure of the following, each of which contains five carbon atoms:

   a. an alkane
   b. an alkene
   c. an alkyne

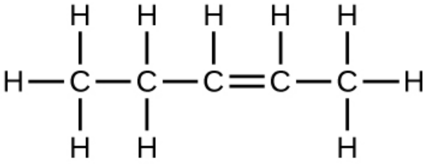
Answer

There are several sets of answers; one is:

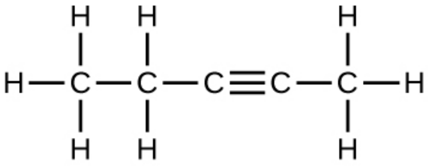
(a) C_5H_{12}



(b) C_5H_{10}



(c) C_5H_8



2. What is the difference between the hybridization of carbon atoms' valence orbitals in saturated and unsaturated hydrocarbons?

3. On a microscopic level, how does the reaction of bromine with a saturated hydrocarbon differ from its reaction with an unsaturated hydrocarbon? How are they similar?

Answer

Both reactions result in bromine being incorporated into the structure of the product. The difference is the way in which that incorporation takes place. In the saturated hydrocarbon, an existing C–H bond is broken, and a bond between the C and the Br can then be formed. In the unsaturated hydrocarbon, the only bond broken in the hydrocarbon is the π bond whose electrons can be used to form a bond to one of the bromine atoms in Br_2 (the electrons from the Br–Br bond form the other C–Br bond on the other carbon that was part of the π bond in the starting unsaturated hydrocarbon).

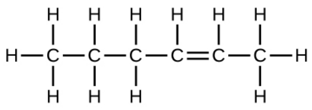
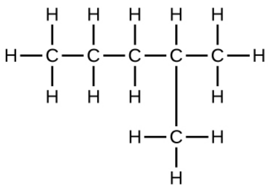
4. On a microscopic level, how does the reaction of bromine with an alkene differ from its reaction with an alkyne? How are they similar?

5. Explain why unbranched alkenes can form geometric isomers while unbranched alkanes cannot. Does this explanation involve the macroscopic domain or the microscopic domain?

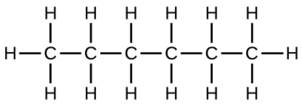
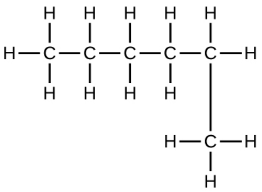
Answer

Unbranched alkanes have free rotation about the C–C bonds, yielding all orientations of the substituents about these bonds equivalent, interchangeable by rotation. In the unbranched alkenes, the inability to rotate about the $\mathrm{C=C}$ bond results in fixed (unchanging) substituent orientations, thus permitting different isomers. Since these concepts pertain to phenomena at the molecular level, this explanation involves the microscopic domain.

6. Explain why these two molecules are not isomers:

7. Explain why these two molecules are not isomers:

Answer

They are the same compound because each is a saturated hydrocarbon containing an unbranched chain of six carbon atoms.

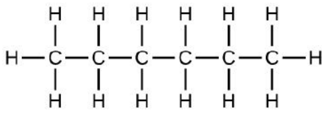
8. How does the carbon-atom hybridization change when polyethylene is prepared from ethylene?

9. Write the Lewis structure and molecular formula for each of the following hydrocarbons:

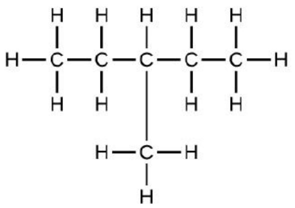
a. hexane
b. 3-methylpentane
c. *cis*-3-hexene
d. 4-methyl-1-pentene
e. 3-hexyne
f. 4-methyl-2-pentyne

Answer

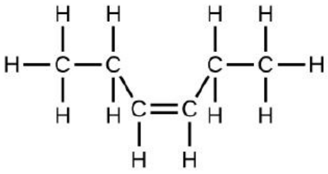
(a) C_6H_{14}



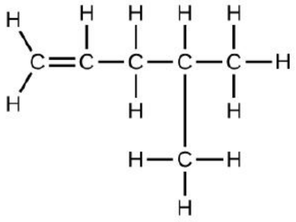
(b) C_6H_{14}



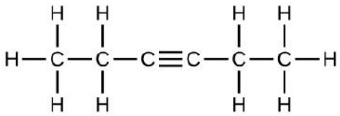
(c) C_6H_{12}



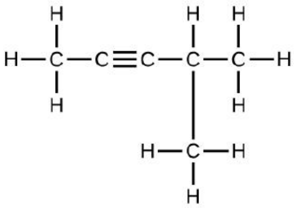
(d) C_6H_{12}



(e) C_6H_{10}



(f) C_6H_{10}

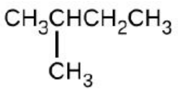


10. Write the chemical formula, condensed formula, and Lewis structure for each of the following hydrocarbons:

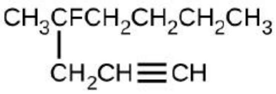
   a. heptane
   b. 3-methylhexane
   c. *trans*-3-heptene
   d. 4-methyl-1-hexene
   e. 2-heptyne
   f. 3,4-dimethyl-1-pentyne

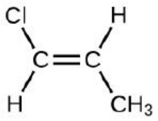
11. Give the complete IUPAC name for each of the following compounds:

   a. $CH_3CH_2CBr_2CH_3$
   b. $(CH_3)_3CCl$

c. 
$CH_3CH(CH_3)CH_2CH_3$

d. \(\mathrm{CH_3CH_2C≡CH\, CH_3CH_2C≡CH}\

e. 
$CH_3CF(CH_2CH{\equiv}CH)CH_2CH_2CH_2CH_3$

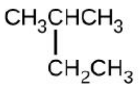
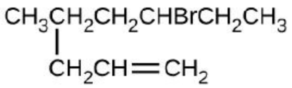
f. 

g. $(CH_3)_2CHCH_2CH=CH_2$

Answer

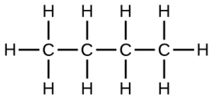
(a) 2,2-dibromobutane; (b) 2-chloro-2-methylpropane; (c) 2-methylbutane; (d) 1-butyne; (e) 4-fluoro-4-methyl-1-octyne; (f) *trans*-1-chloropropene; (g) 5-methyl-1-pentene

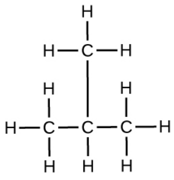
12. Give the complete IUPAC name for each of the following compounds:

a. $(CH_3)_2CHF$
b. $CH_3CHClCHClCH_3$
c. 
$CH_3CH(CH_2CH_3)CH_3$
d. $CH_3CH_2CH=CHCH_3$
e. 
$CH_3CH(CH_2CH=CH_2)CH_2CHBrCH_2CH_3$
f. $(CH_3)_3CCH_2C\equiv CH$

13. Butane is used as a fuel in disposable lighters. Write the Lewis structure for each isomer of butane.

Answer

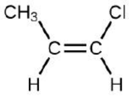

n-butane

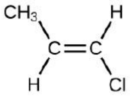

2-methylpropane

14. Write Lewis structures and name the five structural isomers of hexane.

15. Write Lewis structures for the *cis–trans* isomers of $CH_3CH=CHCl$.

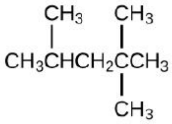
Answer


cis-


trans-

16. Write structures for the three isomers of the aromatic hydrocarbon xylene, $C_6H_4(CH_3)_2$.

17. Isooctane is the common name of the isomer of C_8H_{18} used as the standard of 100 for the gasoline octane rating:

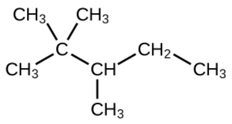


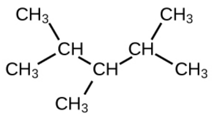
$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_3$$

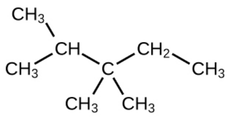
a. What is the IUPAC name for the compound?
b. Name the other isomers that contain a five-carbon chain with three methyl substituents.

Answer

(a) 2,2,4-trimethylpentane; (b) 2,2,3-trimethylpentane, 2,3,4-trimethylpentane, and 2,3,3-trimethylpentane:



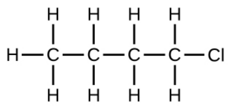




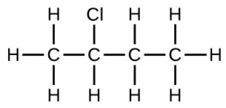
18. Write Lewis structures and IUPAC names for the alkyne isomers of C_4H_6.

19. Write Lewis structures and IUPAC names for all isomers of C_4H_9Cl.

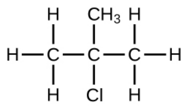
Answer



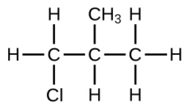
1-chlorobutane



2-chlorobutane



2-chloro-2-methylpropane



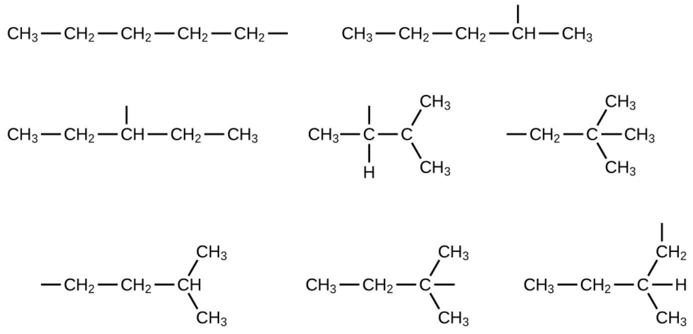
1-chloro-2-methylpropane
(1-chloro-2-methylpropane)

20. Name and write the structures of all isomers of the propyl and butyl alkyl groups.

21. Write the structures for all the isomers of the $–C_5H_{11}$ alkyl group.

Answer

In the following, the carbon backbone and the appropriate number of hydrogen atoms are shown in condensed form:



22. Write Lewis structures and describe the molecular geometry at each carbon atom in the following compounds:

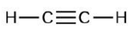
- a. *cis*-3-hexene
- b. *cis*-1-chloro-2-bromoethene
- c. 2-pentyne
- d. *trans*-6-ethyl-7-methyl-2-octene

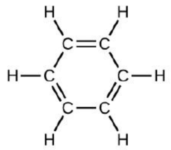
23. Benzene is one of the compounds used as an octane enhancer in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene:

$$3\,C_2H_2 \longrightarrow C_6H_6 \tag{1.10.1}$$

Draw Lewis structures for these compounds, with resonance structures as appropriate, and determine the hybridization of the carbon atoms in each.

Answer





In acetylene, the bonding uses *sp* hybrids on carbon atoms and *s* orbitals on hydrogen atoms. In benzene, the carbon atoms are sp^2 hybridized.

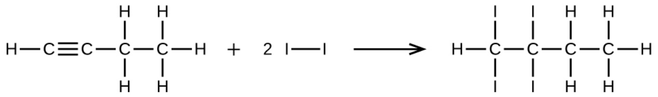
24. Teflon is prepared by the polymerization of tetrafluoroethylene. Write the equation that describes the polymerization using Lewis symbols.

25. Write two complete, balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

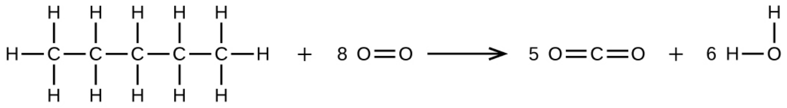
- a. 1 mol of 1-butyne reacts with 2 mol of iodine.
- b. Pentane is burned in air.

Answer

(a) $CH = CCH_2CH_3 + 2I_2 \longrightarrow CHI_2CI_2CH_2CH_3$



(b) $CH_3CH_2CH_2CH_2CH_3 + 8\,O_2 \longrightarrow 5\,CO_2 + 6\,H_2O$



26. Write two complete, balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

a. 2-butene reacts with chlorine.
b. benzene burns in air.

27. What mass of 2-bromopropane could be prepared from 25.5 g of propene? Assume a 100% yield of product.

Answer

65.2 g

28. Acetylene is a very weak acid; however, it will react with moist silver(I) oxide and form water and a compound composed of silver and carbon. Addition of a solution of HCl to a 0.2352-g sample of the compound of silver and carbon produced acetylene and 0.2822 g of AgCl.

a. What is the empirical formula of the compound of silver and carbon?
b. The production of acetylene on addition of HCl to the compound of silver and carbon suggests that the carbon is present as the acetylide ion, C_2^{2-}. Write the formula of the compound showing the acetylide ion.

29. Ethylene can be produced by the pyrolysis of ethane:

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

How many kilograms of ethylene is produced by the pyrolysis of 1.000×10^3 kg of ethane, assuming a 100.0% yield?

Answer

9.328×10^2 kg

CHAPTER OVERVIEW

2: Coordination Chemistry of Transition Metals

2.1: Properties of Transition Metals

Learning Objectives

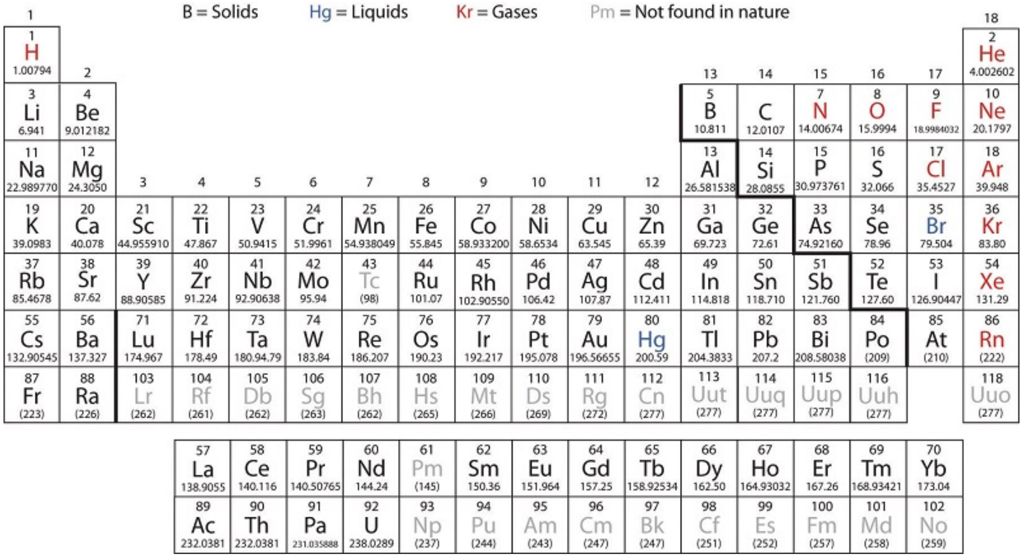
- Locate transition metals on the periodic table
- Describe typical physical and chemical properties of the transition metals

We have daily contact with many transition metals. Iron occurs everywhere—from the rings in your spiral notebook and the cutlery in your kitchen to automobiles, ships, buildings, and in the hemoglobin in your blood. Titanium is useful in the manufacture of lightweight, durable products such as bicycle frames, artificial hips, and jewelry. Chromium is useful as a protective plating on plumbing fixtures and automotive detailing.

Transition metals are defined as those elements that have (or readily form) partially filled *d* orbitals. As shown in Figure 2.1.2, the *d*-block elements in groups 3–11 are transition elements. The *f*-block elements, also called *inner transition metals* (the lanthanides and actinides), also meet this criterion because the *d* orbital is partially occupied before the *f* orbitals. The *d* orbitals fill with the copper family (group 11); for this reason, the next family (group 12) are technically not transition elements. However, the group 12 elements do display some of the same chemical properties and are commonly included in discussions of transition metals. Some chemists do treat the group 12 elements as transition metals.

Figure 2.1.1: Transition metals often form vibrantly colored complexes. The minerals malachite (green), azurite (blue), and proustite (red) are some examples. (credit left: modification of work by James St. John; credit middle: modification of work by Stephanie Clifford; credit right: modification of work by Terry Wallace)

The *d*-block elements are divided into the first transition series (the elements Sc through Cu), the second transition series (the elements Y through Ag), and the third transition series (the element La and the elements Hf through Au). Actinium, Ac, is the first member of the fourth transition series, which also includes Rf through Rg.



B = Solids Hg = Liquids Kr = Gases Pm = Not found in nature

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.00794																	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050											13 Al 26.581538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6534	29 Cu 63.545	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.504	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 107.87	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	71 Lu 174.967	72 Hf 178.49	73 Ta 180.94.79	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.56655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.58038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	103 Lr (262)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (269)	111 Rg (272)	112 Cn (277)	113 Uut (277)	114 Uuq (277)	115 Uup (277)	116 Uuh (277)		118 Uuo (277)

57 La 138.9055	58 Ce 140.116	59 Pr 140.50765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04
89 Ac 232.0381	90 Th 232.0381	91 Pa 231.035888	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)

Figure 2.1.2: The transition metals are located in groups 3–11 of the periodic table. The inner transition metals are in the two rows below the body of the table.

The *f*-block elements are the elements Ce through Lu, which constitute the lanthanide series (or lanthanoid series), and the elements Th through Lr, which constitute the actinide series (or actinoid series). Because lanthanum behaves very much like the lanthanide elements, it is considered a lanthanide element, even though its electron configuration makes it the first member of the third transition series. Similarly, the behavior of actinium means it is part of the actinide series, although its electron configuration makes it the first member of the fourth transition series.

✓ Example 2.1.1: Valence Electrons in Transition Metals

Review how to write electron configurations, covered in the chapter on electronic structure and periodic properties of elements. Recall that for the transition and inner transition metals, it is necessary to remove the *s* electrons before the *d* or *f* electrons. Then, for each ion, give the electron configuration:

a. cerium(III)
b. lead(II)
c. Ti^{2+}
d. Am^{3+}
e. Pd^{2+}

For the examples that are transition metals, determine to which series they belong.

Solution

For ions, the *s*-valence electrons are lost prior to the *d* or *f* electrons.

a. $Ce^{3+}[Xe]4f^1$; Ce^{3+} is an inner transition element in the lanthanide series.
b. $Pb^{2+}[Xe]6s^2 5d^{10} 4f^{14}$; the electrons are lost from the *p* orbital. This is a main group element.
c. titanium(II) $[Ar]3d^2$; first transition series
d. americium(III) $[Rn]5f^6$; actinide
e. palladium(II) $[Kr]4d^8$; second transition series

? Exercise 2.1.1

Check Your Learning Give an example of an ion from the first transition series with no *d* electrons.

Answer

V^{5+} is one possibility. Other examples include Sc^{3+}, Ti^{4+}, Cr^{6+}, and Mn^{7+}.

Uses of Lanthanides in Devices

Lanthanides (elements 57–71) are fairly abundant in the earth’s crust, despite their historic characterization as rare earth elements. Thulium, the rarest naturally occurring lanthanoid, is more common in the earth’s crust than silver (4.5×10^{-5}% versus 0.79×10^{-5}% by mass). There are 17 rare earth elements, consisting of the 15 lanthanoids plus scandium and yttrium. They are called rare because they were once difficult to extract economically, so it was rare to have a pure sample; due to similar chemical properties, it is difficult to separate any one lanthanide from the others. However, newer separation methods, such as ion exchange resins similar to those found in home water softeners, make the separation of these elements easier and more economical. Most ores that contain these elements have low concentrations of all the rare earth elements mixed together.

The commercial applications of lanthanides are growing rapidly. For example, europium is important in flat screen displays found in computer monitors, cell phones, and televisions. Neodymium is useful in laptop hard drives and in the processes that convert crude oil into gasoline (Figure 2.1.3). Holmium is found in dental and medical equipment. In addition, many alternative energy technologies rely heavily on lanthanoids. Neodymium and dysprosium are key components of hybrid vehicle engines and the magnets used in wind turbines.

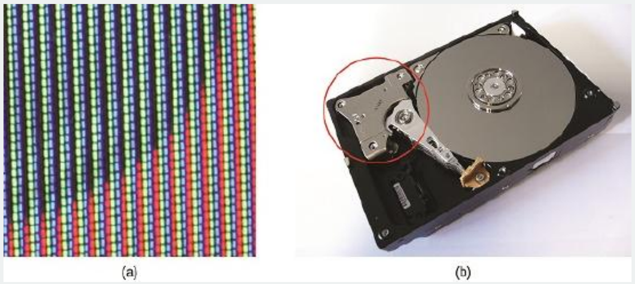


Figure 2.1.3: (a) Europium is used in display screens for televisions, computer monitors, and cell phones. (b) Neodymium magnets are commonly found in computer hard drives. (credit b: modification of work by “KUERT Datenrettung”/Flickr)

> As the demand for lanthanide materials has increased faster than supply, prices have also increased. In 2008, dysprosium cost \$110/kg; by 2014, the price had increased to \$470/kg. Increasing the supply of lanthanoid elements is one of the most significant challenges facing the industries that rely on the optical and magnetic properties of these materials.

The transition elements have many properties in common with other metals. They are almost all hard, high-melting solids that conduct heat and electricity well. They readily form alloys and lose electrons to form stable cations. In addition, transition metals form a wide variety of stable coordination compounds, in which the central metal atom or ion acts as a Lewis acid and accepts one or more pairs of electrons. Many different molecules and ions can donate lone pairs to the metal center, serving as Lewis bases. In this chapter, we shall focus primarily on the chemical behavior of the elements of the first transition series.

2.1.1: Properties of the Transition Elements

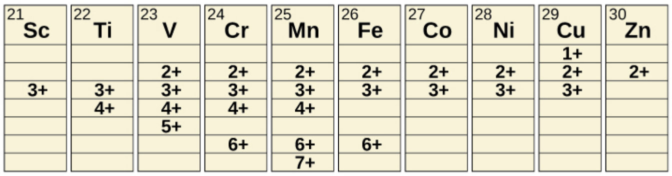
Transition metals demonstrate a wide range of chemical behaviors. As can be seen from their reduction potentials (Table P1), some transition metals are strong reducing agents, whereas others have very low reactivity. For example, the lanthanides all form stable 3+ aqueous cations. The driving force for such oxidations is similar to that of alkaline earth metals such as Be or Mg, forming Be^{2+} and Mg^{2+}. On the other hand, materials like platinum and gold have much higher reduction potentials. Their ability to resist oxidation makes them useful materials for constructing circuits and jewelry.

Ions of the lighter *d*-block elements, such as Cr^{3+}, Fe^{3+}, and Co^{2+}, form colorful hydrated ions that are stable in water. However, ions in the period just below these (Mo^{3+}, Ru^{3+}, and Ir^{2+}) are unstable and react readily with oxygen from the air. The majority of simple, water-stable ions formed by the heavier *d*-block elements are oxyanions such as MoO_4^{2-} and ReO_4^-.

Ruthenium, osmium, rhodium, iridium, palladium, and platinum are the platinum metals. With difficulty, they form simple cations that are stable in water, and, unlike the earlier elements in the second and third transition series, they do not form stable oxyanions.

Both the *d*- and *f*-block elements react with nonmetals to form binary compounds; heating is often required. These elements react with halogens to form a variety of halides ranging in oxidation state from 1+ to 6+. On heating, oxygen reacts with all of the transition elements except palladium, platinum, silver, and gold. The oxides of these latter metals can be formed using other reactants, but they decompose upon heating. The *f*-block elements, the elements of group 3, and the elements of the first transition series except copper react with aqueous solutions of acids, forming hydrogen gas and solutions of the corresponding salts.

Transition metals can form compounds with a wide range of oxidation states. Some of the observed oxidation states of the elements of the first transition series are shown in Figure $2.1.4$. As we move from left to right across the first transition series, we see that the number of common oxidation states increases at first to a maximum towards the middle of the table, then decreases. The values in the table are typical values; there are other known values, and it is possible to synthesize new additions. For example, in 2014, researchers were successful in synthesizing a new oxidation state of iridium (9+).



21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
								1+	
		2+	2+	2+	2+	2+	2+	2+	2+
3+	3+	3+	3+	3+	3+	3+	3+	3+	
	4+	4+	4+	4+					
		5+							
			6+	6+	6+				
				7+					

Figure $2.1.4$:Transition metals of the first transition series can form compounds with varying oxidation states.

For the elements scandium through manganese (the first half of the first transition series), the highest oxidation state corresponds to the loss of all of the electrons in both the *s* and *d* orbitals of their valence shells. The titanium(IV) ion, for example, is formed when the titanium atom loses its two 3*d* and two 4*s* electrons. These highest oxidation states are the most stable forms of scandium, titanium, and vanadium. However, it is not possible to continue to remove all of the valence electrons from metals as we continue through the series. Iron is known to form oxidation states from 2+ to 6+, with iron(II) and iron(III) being the most common. Most of the elements of the first transition series form ions with a charge of 2+ or 3+ that are stable in water, although those of the early members of the series can be readily oxidized by air.

The elements of the second and third transition series generally are more stable in higher oxidation states than are the elements of the first series. In general, the atomic radius increases down a group, which leads to the ions of the second and third series being larger than are those in the first series. Removing electrons from orbitals that are located farther from the nucleus is easier than removing electrons close to the nucleus. For example, molybdenum and tungsten, members of group 6, are limited mostly to an oxidation state of 6+ in aqueous solution. Chromium, the lightest member of the group, forms stable Cr^{3+} ions in water and, in the absence of air, less stable Cr^{2+} ions. The sulfide with the highest oxidation state for chromium is Cr_2S_3, which contains the Cr^{3+} ion. Molybdenum and tungsten form sulfides in which the metals exhibit oxidation states of 4+ and 6+.

✓ Example 2.1.2: Activity of the Transition Metals

Which is the strongest oxidizing agent in acidic solution: dichromate ion, which contains chromium(VI), permanganate ion, which contains manganese(VII), or titanium dioxide, which contains titanium(IV)?

Solution

First, we need to look up the reduction half reactions (Table P1) for each oxide in the specified oxidation state:

$$\mathrm{Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O} \quad +1.33\ \mathrm{V} \tag{2.1.1}$$

$$\mathrm{MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + H_2O} \quad +1.51\ \mathrm{V} \tag{2.1.2}$$

$$\mathrm{TiO_2 + 4\,H^+ + 2\,e^- \longrightarrow Ti^{2+} + 2\,H_2O} \quad -0.50\ \mathrm{V} \tag{2.1.3}$$

A larger reduction potential means that it is easier to reduce the reactant. Permanganate, with the largest reduction potential, is the strongest oxidizer under these conditions. Dichromate is next, followed by titanium dioxide as the weakest oxidizing agent (the hardest to reduce) of this set.

? Exercise 2.1.2

Predict what reaction (if any) will occur between HCl and Co(*s*), and between HBr and Pt(*s*). You will need to use the standard reduction potentials from (Table P1).

Answer

$\mathrm{Co}(s) + 2\,\mathrm{HCl} \longrightarrow \mathrm{H_2} + \mathrm{CoCl_2}(aq)$; no reaction because Pt(*s*) will not be oxidized by H^+

2.1.2: Preparation of the Transition Elements

Ancient civilizations knew about iron, copper, silver, and gold. The time periods in human history known as the Bronze Age and Iron Age mark the advancements in which societies learned to isolate certain metals and use them to make tools and goods. Naturally occurring ores of copper, silver, and gold can contain high concentrations of these metals in elemental form (Figure 2.1.5). Iron, on the other hand, occurs on earth almost exclusively in oxidized forms, such as rust (Fe_2O_3). The earliest known iron implements were made from iron meteorites. Surviving iron artifacts dating from approximately 4000 to 2500 BC are rare, but all known examples contain specific alloys of iron and nickel that occur only in extraterrestrial objects, not on earth. It took thousands of years of technological advances before civilizations developed iron smelting, the ability to extract a pure element from its naturally occurring ores and for iron tools to become common.

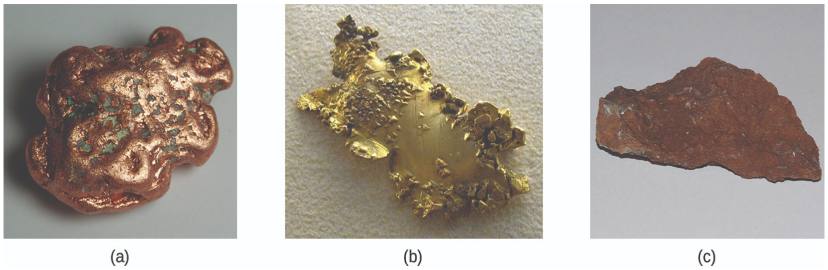


Figure 2.1.5: Transition metals occur in nature in various forms. Examples include (a) a nugget of copper, (b) a deposit of gold, and (c) an ore containing oxidized iron. (credit a: modification of work by http://images-of-elements.com/copper-2.jpg; credit c: modification of work by http://images-of-elements.com/iron-ore.jpg)

Generally, the transition elements are extracted from minerals found in a variety of ores. However, the ease of their recovery varies widely, depending on the concentration of the element in the ore, the identity of the other elements present, and the difficulty of reducing the element to the free metal.

In general, it is not difficult to reduce ions of the *d*-block elements to the free element. Carbon is a sufficiently strong reducing agent in most cases. However, like the ions of the more active main group metals, ions of the *f*-block elements must be isolated by electrolysis or by reduction with an active metal such as calcium.

2.1.3: High Temperature Superconductors

A superconductor is a substance that conducts electricity with no resistance. This lack of resistance means that there is no energy loss during the transmission of electricity. This would lead to a significant reduction in the cost of electricity.

Most currently used, commercial superconducting materials, such as NbTi and Nb_3Sn, do not become superconducting until they are cooled below 23 K (−250 °C). This requires the use of liquid helium, which has a boiling temperature of 4 K and is expensive and difficult to handle. The cost of liquid helium has deterred the widespread application of superconductors.

One of the most exciting scientific discoveries of the 1980s was the characterization of compounds that exhibit superconductivity at temperatures above 90 K. (Compared to liquid helium, 90 K is a high temperature.) Typical among the high-temperature superconducting materials are oxides containing yttrium (or one of several rare earth elements), barium, and copper in a 1:2:3 ratio. The formula of the ionic yttrium compound is $YBa_2Cu_3O_7$.

The new materials become superconducting at temperatures close to 90 K (Figure 2.1.10), temperatures that can be reached by cooling with liquid nitrogen (boiling temperature of 77 K). Not only are liquid nitrogen-cooled materials easier to handle, but the cooling costs are also about 1000 times lower than for liquid helium.

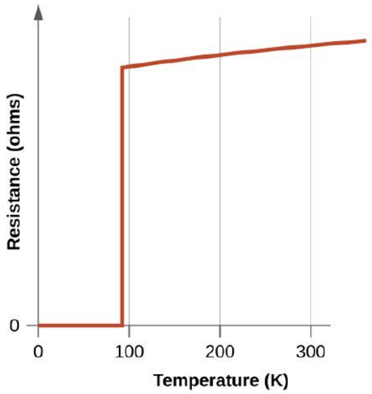


Figure 2.1.10: The resistance of the high-temperature superconductor $YBa_2Cu_3O_7$ varies with temperature. Note how the resistance falls to zero below 92 K, when the substance becomes superconducting.

Although the brittle, fragile nature of these materials presently hampers their commercial applications, they have tremendous potential that researchers are hard at work improving their processes to help realize. Superconducting transmission lines would carry current for hundreds of miles with no loss of power due to resistance in the wires. This could allow generating stations to be located in areas remote from population centers and near the natural resources necessary for power production. The first project demonstrating the viability of high-temperature superconductor power transmission was established in New York in 2008.

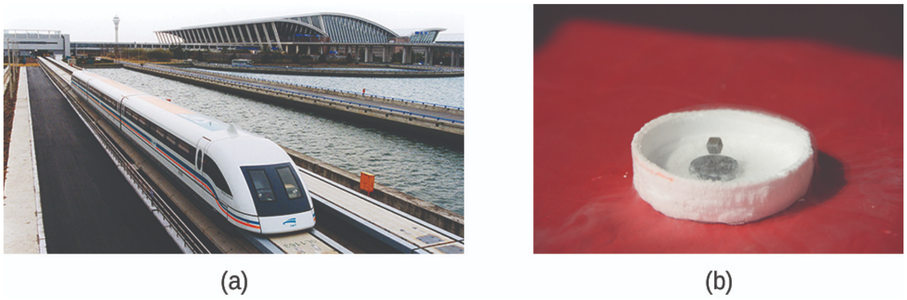


Figure 2.1.11: (a) This magnetic levitation train (or maglev) uses superconductor technology to move along its tracks. (b) A magnet can be levitated using a dish like this as a superconductor. (credit a: modification of work by Alex Needham; credit b: modification of work by Kevin Jarrett)

Researchers are also working on using this technology to develop other applications, such as smaller and more powerful microchips. In addition, high-temperature superconductors can be used to generate magnetic fields for applications such as medical devices, magnetic levitation trains, and containment fields for nuclear fusion reactors (Figure 2.1.11).

Video 2.1.1: Watch how a high-temperature superconductor levitates around a magnetic racetrack in the video.

Summary

The transition metals are elements with partially filled *d* orbitals, located in the *d*-block of the periodic table. The reactivity of the transition elements varies widely from very active metals such as scandium and iron to almost inert elements, such as the platinum metals.

Transition metals exhibit chemical behavior typical of metals. Most transition metals form a variety of stable oxidation states, allowing them to demonstrate a wide range of chemical reactivity.

Glossary

actinide series

(also, actinoid series) actinium and the elements in the second row or the *f*-block, atomic numbers 89–103

***d*-block element**

one of the elements in groups 3–11 with valence electrons in *d* orbitals

***f*-block element**

(also, inner transition element) one of the elements with atomic numbers 58–71 or 90–103 that have valence electrons in *f* orbitals; they are frequently shown offset below the periodic table

first transition series

transition elements in the fourth period of the periodic table (first row of the *d*-block), atomic numbers 21–29

fourth transition series

transition elements in the seventh period of the periodic table (fourth row of the *d*-block), atomic numbers 89 and 104–111

lanthanide series

(also, lanthanoid series) lanthanum and the elements in the first row or the *f*-block, atomic numbers 57–71

platinum metals

group of six transition metals consisting of ruthenium, osmium, rhodium, iridium, palladium, and platinum that tend to occur in the same minerals and demonstrate similar chemical properties

rare earth element

collection of 17 elements including the lanthanides, scandium, and yttrium that often occur together and have similar chemical properties, making separation difficult

second transition series

transition elements in the fifth period of the periodic table (second row of the *d*-block), atomic numbers 39–47

superconductor

material that conducts electricity with no resistance

third transition series

transition elements in the sixth period of the periodic table (third row of the *d*-block), atomic numbers 57 and 72–79

Contributors and Attributions

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2.2: Coordination Chemistry of Transition Metals

Learning Objectives

- List the defining traits of coordination compounds
- Determine the coordination number and oxidation state of the central metal ion in a coordination complex
- Distinguish between monodentate and polydentate ligands
- Identify several natural and technological occurrences of coordination compounds

The hemoglobin in your blood, the chlorophyll in green plants, vitamin B_{12}, and the catalyst used in the manufacture of polyethylene all contain coordination compounds. Ions of the metals, especially the transition metals, are likely to form complexes. Many of these compounds are highly colored (Figure $2.2.1$). In the remainder of this chapter, we will consider the structure and bonding of these remarkable compounds.

Figure $2.2.1$: Metal ions that contain partially filled d subshell usually form colored complex ions; ions with empty d subshell (d^0) or with filled d subshells (d^{10}) usually form colorless complexes. This figure shows, from left to right, solutions containing $[M(H_2O)_6]^{n+}$ ions with M = $Sc^{3+}(d^0)$, $Cr^{3+}(d^3)$, $Co^{2+}(d^7)$, $Ni^{2+}(d^8)$, $Cu^{2+}(d^9)$, and $Zn^{2+}(d^{10})$. (credit: Sahar Atwa)

Remember that in most main group element compounds, the valence electrons of the isolated atoms combine to form chemical bonds that satisfy the octet rule. For instance, the four valence electrons of carbon overlap with electrons from four hydrogen atoms to form CH_4. The one valence electron leaves sodium and adds to the seven valence electrons of chlorine to form the ionic formula unit NaCl (Figure $2.2.2$). Transition metals do not normally bond in this fashion. They primarily form coordinate covalent bonds, a form of the Lewis acid-base interaction in which both of the electrons in the bond are contributed by a donor (Lewis base) to an electron acceptor (Lewis acid). The Lewis acid in coordination complexes, often called a central metal ion (or atom), is often a transition metal or inner transition metal, although main group elements can also form coordination compounds. The Lewis base donors, called ligands, can be a wide variety of chemicals—atoms, molecules, or ions. The only requirement is that they have one or more electron pairs, which can be donated to the central metal. Most often, this involves a donor atom with a lone pair of electrons that can form a coordinate bond to the metal.

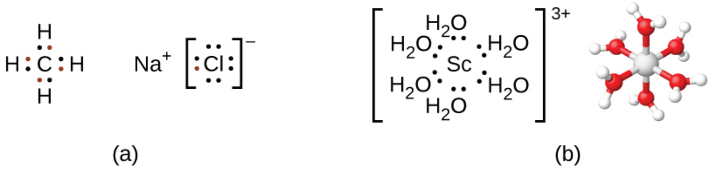


Figure $2.2.2$: (a) Covalent bonds involve the sharing of electrons, and ionic bonds involve the transferring of electrons associated with each bonding atom, as indicated by the colored electrons. (b) However, coordinate covalent bonds involve electrons from a Lewis base being donated to a metal center. The lone pairs from six water molecules form bonds to the scandium ion to form an octahedral complex. (Only the donated pairs are shown.)

2.2.1: Coordination Number

The coordination sphere consists of the central metal ion or atom plus its attached ligands. Brackets in a formula enclose the coordination sphere; species outside the brackets are not part of the coordination sphere. The **coordination number** of the central metal ion or atom is the number of donor atoms bonded to it. The coordination number for the silver ion in $[Ag(NH_3)_2]^+$ is two (Figure $2.2.3$). For the copper(II) ion in $[CuCl_4]^{2-}$, the coordination number is four, whereas for the cobalt(II) ion in $[Co(H_2O)_6]^{2+}$ the coordination number is six. Each of these ligands is monodentate, from the Greek for "one toothed," meaning that they connect with the central metal through only one atom. In this case, the number of ligands and the coordination number are equal.

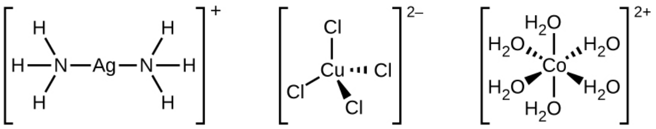


Figure 2.2.3: The complexes (a) $[Ag(NH_3)_2]^+$, (b) $[Cu(Cl)_4]^{2-}$, and (c) $[Co(H_2O)_6]^{2+}$ have coordination numbers of two, four, and six, respectively. The geometries of these complexes are the same as we have seen with VSEPR theory for main group elements: linear, tetrahedral, and octahedral.

Many other ligands coordinate to the metal in more complex fashions. Bidentate ligands are those in which two atoms coordinate to the metal center. For example, ethylenediamine (en, $H_2NCH_2CH_2NH_2$) contains two nitrogen atoms, each of which has a lone pair and can serve as a Lewis base (Figure 2.2.4). Both of the atoms can coordinate to a single metal center. In the complex $[Co(en)_3]^{3+}$, there are three bidentate en ligands, and the coordination number of the cobalt(III) ion is six. The most common coordination numbers are two, four, and six, but examples of all coordination numbers from 1 to 15 are known.

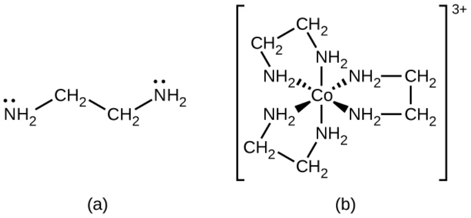


Figure 2.2.4: (a) The ethylenediamine (en) ligand contains two atoms with lone pairs that can coordinate to the metal center. (b) The cobalt(III) complex $[Co(en)_3]^{3+}$ *contains three of these ligands, each forming two bonds to the cobalt ion.*

Any ligand that bonds to a central metal ion by more than one donor atom is a polydentate ligand (or “many teeth”) because it can "bite" into the metal center with more than one bond. The term chelate (pronounced “KEY-late”) from the Greek for “claw” is also used to describe this type of interaction. Many polydentate ligands are chelating ligands, and a complex consisting of one or more of these ligands and a central metal is a chelate. A chelating ligand is also known as a chelating agent. A chelating ligand holds the metal ion rather like a crab’s claw would hold a marble. Figure 2.2.4 showed one example of a chelate and the heme complex in hemoglobin is another important example (Figure 2.2.5). It contains a polydentate ligand with four donor atoms that coordinate to iron.

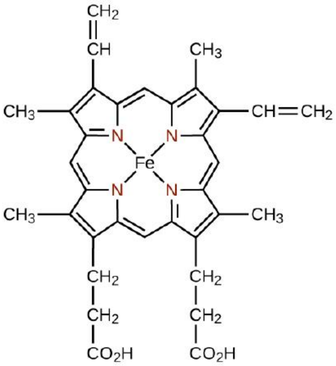


Figure 2.2.5: The single ligand heme contains four nitrogen atoms that coordinate to iron in hemoglobin to form a chelate.

Polydentate ligands are sometimes identified with prefixes that indicate the number of donor atoms in the ligand. As we have seen, ligands with one donor atom, such as NH_3, Cl^-, and H_2O, are monodentate ligands. Ligands with two donor groups are bidentate ligands. Ethylenediamine, $H_2NCH_2CH_2NH_2$, and the anion of the acid glycine, $NH_2CH_2CO_2^-$ (Figure 2.2.6) are examples of bidentate ligands. Tridentate ligands, tetradentate ligands, pentadentate ligands, and hexadentate ligands contain three, four, five, and six donor atoms, respectively. The heme ligand (Figure 2.2.5) is a tetradentate ligand.

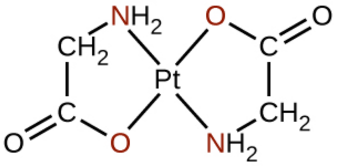


Figure 2.2.6: Each of the anionic ligands shown attaches in a bidentate fashion to platinum(II), with both a nitrogen and oxygen atom coordinating to the metal.

2.2.2: Oxidation State

The oxidation state of the metal is determined based on the charges of each ligand and the overall charge of the coordination compound. For example, in $[Cr(H_2O)_4Cl_2]Br$, the coordination sphere (in brackets) has a charge of 1+ to balance the bromide ion. The water ligands are neutral, and the chloride ligands are anionic with a charge of 1− each. To determine the oxidation state of the metal, we set the overall charge equal to the sum of the ligands and the metal: $+1 = -2 + x$, so the oxidation state (x) is equal to 3+.

✓ Example 2.2.1: Coordination Numbers and Oxidation States

Determine the name of the following complexes and give the coordination number of the central metal atom.

a. $Na_2[PtCl_6]$
b. $K_3[Fe(C_2O_4)_3]$
c. $[Co(NH_3)_5Cl]Cl_2$

Solution

a. There are two Na^+ ions, so the coordination sphere has a negative two charge: $[PtCl_6]^{2-}$. There are six anionic chloride ligands, so $-2 = -6 + x$, and the oxidation state of the platinum is 4+. The name of the complex is sodium hexachloroplatinate(IV), and the coordination number is six.
b. The coordination sphere has a charge of 3− (based on the potassium) and the oxalate ligands each have a charge of 2−, so the metal oxidation state is given by $-3 = -6 + x$, and this is an iron(III) complex. The name is potassium trisoxalatoferrate(III) (note that tris is used instead of tri because the ligand name starts with a vowel). Because oxalate is a bidentate ligand, this complex has a coordination number of six.
c. In this example, the coordination sphere has a cationic charge of 2+. The NH_3 ligand is neutral, but the chloro ligand has a charge of 1−. The oxidation state is found by $+2 = -1 + x$ and is 3+, so the complex is pentaaminechlorocobalt(III) chloride and the coordination number is six.

? Exercise 2.2.1

The $K[Ag(CN)_2]$ complex is used to make antiseptic compounds. Give the coordination number and the oxidation state of the metal.

Answer

coordination number two, oxidation state +1

2.2.3: Coordination Complexes in Nature and Technology

Chlorophyll, the green pigment in plants, is a complex that contains magnesium (Figure 2.2.7). This is an example of a main group element in a coordination complex. Plants appear green because chlorophyll absorbs red and purple light; the reflected light consequently appears green. The energy resulting from the absorption of light is used in photosynthesis.

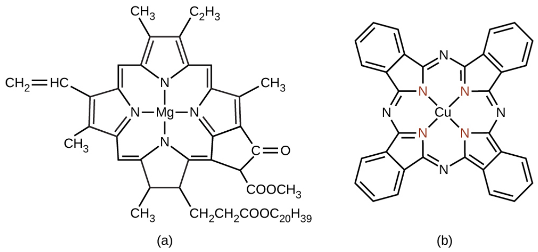


Figure 2.2.7: (a) Chlorophyll comes in several different forms, which all have the same basic structure around the magnesium center. (b) Copper phthalocyanine blue, a square planar copper complex, is present in some blue dyes.

One of the most important applications of transition metals is as industrial catalysts. As you will learn in the chapter on kinetics, a catalyst increases the rate of reaction by lowering the activation energy and is regenerated in the catalytic cycle. Over 90% of all manufactured products are made with the aid of one or more catalysts. The ability to bind ligands and change oxidation states makes transition metal catalysts well suited for catalytic applications. Vanadium oxide is used to produce 230,000,000 tons of sulfuric acid worldwide each year, which in turn is used to make everything from fertilizers to cans for food. Plastics are made with the aid of transition metal catalysts, along with detergents, fertilizers, paints, and more (Figure 2.2.8). Very complicated pharmaceuticals are manufactured with catalysts that are selective, reacting with one specific bond out of a large number of possibilities. Catalysts allow processes to be more economical and more environmentally friendly. Developing new catalysts and better understanding of existing systems are important areas of current research.

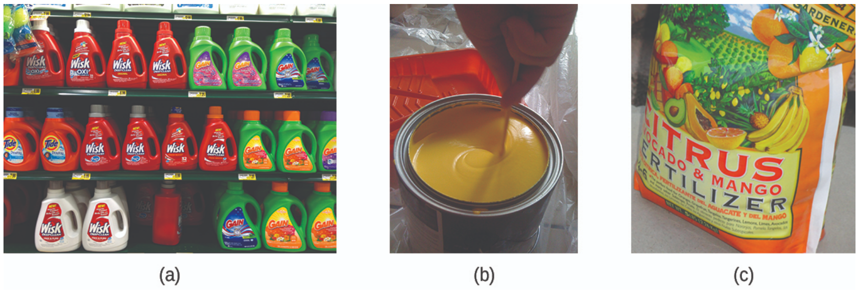


Figure 2.2.8: (a) Detergents, (b) paints, and (c) fertilizers are all made using transition metal catalysts. (credit a: modification of work by "Mr. Brian"/Flickr; credit b: modification of work by Ewen Roberts; credit c: modification of work by "osseous"/Flickr)

Many other coordination complexes are also brightly colored. The square planar copper(II) complex phthalocyanine blue (from Figure 2.2.7) is one of many complexes used as pigments or dyes. This complex is used in blue ink, blue jeans, and certain blue paints.

The structure of heme (Figure 2.2.8), the iron-containing complex in hemoglobin, is very similar to that in chlorophyll. In hemoglobin, the red heme complex is bonded to a large protein molecule (globin) by the attachment of the protein to the heme ligand. Oxygen molecules are transported by hemoglobin in the blood by being bound to the iron center. When the hemoglobin loses its oxygen, the color changes to a bluish red. Hemoglobin will only transport oxygen if the iron is Fe^{2+}; oxidation of the iron to Fe^{3+} prevents oxygen transport.

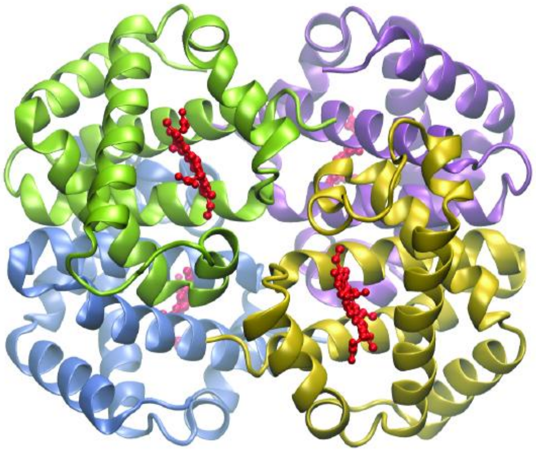


Figure 2.2.8: Hemoglobin contains four protein subunits, each of which has an iron center attached to a heme ligand (shown in red), which is coordinated to a globin protein. Each subunit is shown in a different color.

Complexing agents often are used for water softening because they tie up such ions as Ca^{2+}, Mg^{2+}, and Fe^{2+}, which make water hard. Many metal ions are also undesirable in food products because these ions can catalyze reactions that change the color of food. Coordination complexes are useful as preservatives. For example, the ligand EDTA, $(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2$, coordinates to metal ions through six donor atoms and prevents the metals from reacting (Figure 2.2.9). This ligand also is used to sequester metal ions in paper production, textiles, and detergents, and has pharmaceutical uses.

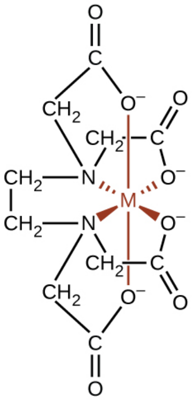


Figure 2.2.9: The ligand EDTA binds tightly to a variety of metal ions by forming hexadentate complexes.

Complexing agents that tie up metal ions are also used as drugs. British Anti-Lewisite (BAL), $HSCH_2CH(SH)CH_2OH$, is a drug developed during World War I as an antidote for the arsenic-based war gas Lewisite. BAL is now used to treat poisoning by heavy metals, such as arsenic, mercury, thallium, and chromium. The drug is a ligand and functions by making a water-soluble chelate of the metal; the kidneys eliminate this metal chelate (Figure 2.2.10). Another polydentate ligand, enterobactin, which is isolated from certain bacteria, is used to form complexes of iron and thereby to control the severe iron buildup found in patients suffering from blood diseases such as Cooley's anemia, who require frequent transfusions. As the transfused blood breaks down, the usual metabolic processes that remove iron are overloaded, and excess iron can build up to fatal levels. Enterobactin forms a water-soluble complex with excess iron, and the body can safely eliminate this complex.

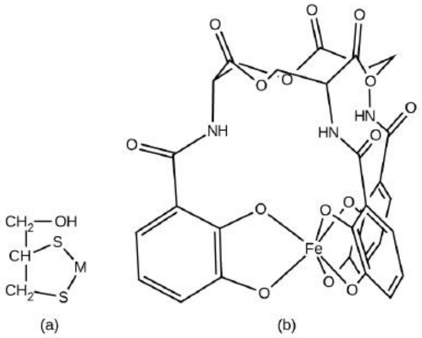


Figure 2.2.10: Coordination complexes are used as drugs. (a) British Anti-Lewisite is used to treat heavy metal poisoning by coordinating metals (M), and enterobactin (b) allows excess iron in the blood to be removed.

✓ Example 2.2.3: Chelation Therapy

Ligands like BAL and enterobactin are important in medical treatments for heavy metal poisoning. However, chelation therapies can disrupt the normal concentration of ions in the body, leading to serious side effects, so researchers are searching for new chelation drugs. One drug that has been developed is dimercaptosuccinic acid (DMSA), shown in Figure 2.2.11. Identify which atoms in this molecule could act as donor atoms.

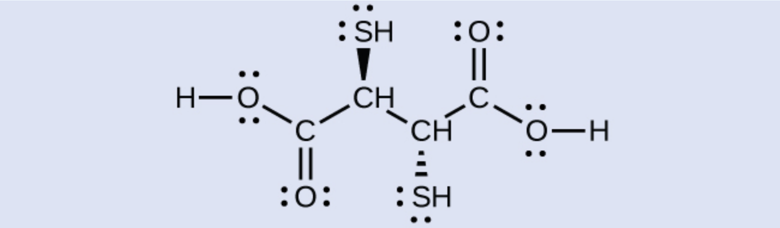


Figure 2.2.11: Dimercaptosuccinic acid is used to treat heavy metal poisoning.

Solution

All of the oxygen and sulfur atoms have lone pairs of electrons that can be used to coordinate to a metal center, so there are six possible donor atoms. Geometrically, only two of these atoms can be coordinated to a metal at once. The most common binding mode involves the coordination of one sulfur atom and one oxygen atom, forming a five-member ring with the metal.

Exercise 2.2.3

Some alternative medicine practitioners recommend chelation treatments for ailments that are not clearly related to heavy metals, such as cancer and autism, although the practice is discouraged by many scientific organizations.[1] Identify at least two biologically important metals that could be disrupted by chelation therapy.

Answer

Ca, Fe, Zn, and Cu

Ligands are also used in the electroplating industry. When metal ions are reduced to produce thin metal coatings, metals can clump together to form clusters and nanoparticles. When metal coordination complexes are used, the ligands keep the metal atoms isolated from each other. It has been found that many metals plate out as a smoother, more uniform, better-looking, and more adherent surface when plated from a bath containing the metal as a complex ion. Thus, complexes such as $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ are used extensively in the electroplating industry.

In 1965, scientists at Michigan State University discovered that there was a platinum complex that inhibited cell division in certain microorganisms. Later work showed that the complex was *cis*-diaminedichloroplatinum(II), $[Pt(NH_3)_2(Cl)_2]$, and that the *trans* isomer was not effective. The inhibition of cell division indicated that this square planar compound could be an anticancer agent. In 1978, the US Food and Drug Administration approved this compound, known as cisplatin, for use in the treatment of certain forms of cancer. Since that time, many similar platinum compounds have been developed for the treatment of cancer. In all cases, these are the *cis* isomers and never the *trans* isomers. The diamine $(NH_3)_2$ portion is retained with other groups, replacing the dichloro $[(Cl)_2]$ portion. The newer drugs include carboplatin, oxaliplatin, and satraplatin.

Contributors and Attributions

Summary

The transition elements and main group elements can form coordination compounds, or complexes, in which a central metal atom or ion is bonded to one or more ligands by coordinate covalent bonds. Ligands with more than one donor atom are called polydentate ligands and form chelates. Coordination complexes have a wide variety of uses including oxygen transport in blood, water purification, and pharmaceutical use.

2.2.4: Footnotes

1. National Council against Health Fraud, *NCAHF Policy Statement on Chelation Therapy*, (Peabody, MA, 2002).

Glossary

bidentate ligand

ligand that coordinates to one central metal through coordinate bonds from two different atoms

central metal

ion or atom to which one or more ligands is attached through coordinate covalent bonds

chelate

complex formed from a polydentate ligand attached to a central metal

chelating ligand

ligand that attaches to a central metal ion by bonds from two or more donor atoms

***cis* configuration**

configuration of a geometrical isomer in which two similar groups are on the same side of an imaginary reference line on the molecule

coordination compound

substance consisting of atoms, molecules, or ions attached to a central atom through Lewis acid-base interactions

coordination number

number of coordinate covalent bonds to the central metal atom in a complex or the number of closest contacts to an atom in a crystalline form

coordination sphere

central metal atom or ion plus the attached ligands of a complex

donor atom

atom in a ligand with a lone pair of electrons that forms a coordinate covalent bond to a central metal

ionization isomer

(or coordination isomer) isomer in which an anionic ligand is replaced by the counter ion in the inner coordination sphere

ligand

ion or neutral molecule attached to the central metal ion in a coordination compound

linkage isomer

coordination compound that possesses a ligand that can bind to the transition metal in two different ways (CN^- vs. NC^-)

monodentate

ligand that attaches to a central metal through just one coordinate covalent bond

optical isomer

(also, enantiomer) molecule that is a nonsuperimposable mirror image with identical chemical and physical properties, except when it reacts with other optical isomers

polydentate ligand

ligand that is attached to a central metal ion by bonds from two or more donor atoms, named with prefixes specifying how many donors are present (e.g., hexadentate = six coordinate bonds formed)

trans **configuration**

configuration of a geometrical isomer in which two similar groups are on opposite sides of an imaginary reference line on the molecule

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).

2.3: Nomenclature for Coordination Compounds

The name of a coordination compound must communicate several things: the number and identity of ligands present, counterions, metal identity, and oxidation state. You'll notice that the names for coordination compounds tend to be quite complex.

Ligand Prefixes

Ligands are named as a prefix to the central metal ion name. In Table $2.3.1$, the prefixes used for several common ligands are listed. In general, if the ligand is an anion ending in "-ide", the "-ide" is converted into "-o". (Recent changes to IUPAC naming rules favor dropping only the "e" and replacing it with "o". For example, "fluoride" would become "fluorido-".) When the anion ends in "-ate", then the "e" is dropped and replaced with an "-o" (e.g. oxalate becomes oxalato).

When the ligand is a neutral, the general rule is to keep the name of the compound. A few common ligands are exceptions to this that you must memorize. These are H_2O (called aqua), NH_3 (called ammine), CO (called carbonyl), and NO (called nitrosyl).

Table $2.3.1$. *Common Ligands and their Prefixes for Coordination Compounds*

Ligand	**Prefix**
F^-	fluoro
Cl^-	chloro
Br^-	bromo
I^-	iodo
CN^-	cyano
NO_3^-	nitrato
OH^-	hydroxo
O^{2-}	oxo
$C_2O_4^{2-}$	oxalato
CO_2^{2-}	carbonato
H_2O	aqua
NH_3	ammine
CO	carbonyl
NO	nitrosyl
$NH_2CH_2CH_2NH_2$	ethylenediamine

We need to communicate not only the identity of the ligand(s), but the number of each present. To indicate the number of a particular ligand we use Greek prefixes (Table $2.3.2$).

Table $2.3.2$. *Greek prefixes associated with the number of ligands in a coordination compound.*

Number	2	3	4	5	6
Prefix	di	tri	tetra	penta	hexa

Nomenclature of Complexes with Anionic Coordination Spheres

We can now develop the full name of a coordination compound. Let us consider compounds with complex anions first. We can name them according to three steps.

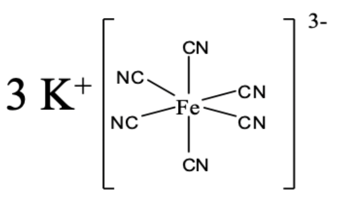
1. Name the counter cation. We do not account for the number of counter cations in the name.

2. Determine the name and the number of ligands. If the ligand is anionic it gets the suffix “o”. Generally, when an anion ends with “-ide”, the “-ide” is omitted, and replaced by “-o”. The greek numerical prefix will immediately precede the name of the ligand. For example, if there are three chloride ligands, the name would contain "trichloro-".

3. Name the metal ion and add the suffix “ate” to the name. You add the oxidation number of the metal in roman numerals after the name of the metal. Note that if the element symbol of the metal is derived from a latin name then the latin name is used. For example if silver is the metal then the complex anion is an argentate, if lead is the metal the complex anion is a plumbate. Also here abbreviations are often used to make pronunciation easier. If the name ends with “um” that ending is replaced by “ate”.

Example 2.3.1

Name this coordination compound.



Solution

There are three K$^+$ cations, so the name starts with potassium. We realize next, that there are six cyanide anions as ligands, so the name continues “hexacyano”. The name of the metal is iron, but we use the latin name ferrum, and replace the ending “um” with the ending “ate”. The oxidation number of the iron is +3. We can see that from the fact that the complex ion has a 3- charge, and the six cyano ligands have a 1- charge each.

So overall it would be either a potassium hexacyanoferrate (III).

Exercise 2.3.1

How would you name this complex?

$$H_2[PtCl_6]$$

Answer

First, we need to name the cation. What is it? It is just “hydrogen”. Next we need to determine the name and number of ligands. We have six chloro ligands, so the name continues with “hexachloro”. The name of metal is platinum. We replace the ending “um” by “ate”. The roman numeral would be (IV) because the oxidation state of the Pt is +4. We can see this from the fact that the complex anion has a 2- charge, and the six chloro ligands have a 1- charge each. We must add +4 to -6 to get to -2.

Therefore, the name would be hydrogen hexachloroplatinate (IV).

Exercise 2.3.2

How would you name this complex?

$$K_3[Ag(S_2O_3)_2]$$

Answer

This example has three K$^+$ cations, so the name starts with potassium. What is the name of the ligand? The name of the anion is thiosulfate. In this case we replace the ending “e” by the ending “o”. We have two ligands, so it is a “dithiosulfato”. The metal is silver, but we use the latin name “argentum”, and replace the ending “um” by the ending “ate”. So it is an “argentate” . Fusing the parts together gives “potassium dithiosulfato argentate”. The oxidation number of Ag is +1, the charge at the anion is -3.

Therefore the name would be potassium dithiosulfatoargenate (I).

Nomenclature of Complexes with Cationic Coordination Spheres

Now let us name complexes with complex cations. We name the complex cation first, and then the anion. Then, we determine the name and the number of the ligands and prefixes accordingly. If there is an anionic ligand we give it the suffix “o” again. Then, we name the metal. In this case, we always use English names. As before, we place the oxidation number in roman numerals.

Example 2.3.2

Name the coordination compound here.

$$\left[\ H_3N\text{—}Ag\text{—}NH_3\ \right]^{+} \qquad Cl^{-}$$

Solution

There are two NH_3 ligands which are neutral. We have to consider that NH_3 as a ligand is called an “ammine” ligand. Note that it is spelled with two “m” in the middle. So the name starts “diammine”. The name of the metal is silver, and the oxidation state of silver is +1. This is because the complex has a 1+ charge and the ammine ligands are neutral. The anion is a chloride anion.

Therefore then name would be diamminesilver (I) chloride.

Exercise 2.3.3

Name this coordination compound.

$$[Pt(NH_3)_4]\ Cl_2$$

Answer

The complex has four NH_3 ligands, so the name starts with tetraammine. Platinum is the metal, so the name continues “platinum”. The oxidation state of Pt is +2 because the complex cation has a 2+ charge, and the ligands are charge-neutral. The name of the anion is “choride”.

So overall it is a tetraammineplatinum (II) chloride.

Exercise 2.3.4

Name this coordination compound.

$$[Ni(H_2O)_6]\ Cl_2$$

Answer

The complex has six water ligands, therefore the name starts with “hexaaqua” followed by the name of the metal with is “nickel”. The oxidation state of Ni is 2+ because the charge at the complex cation is +2, and the ligands are charge-neutral. The name of the anion is “chloride”.

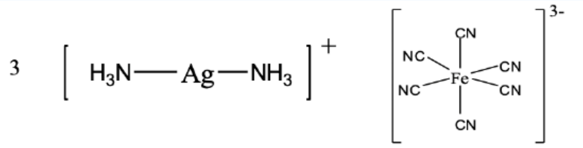
Therefore, the name is hexaaaquanickel (II) chloride.

Nomenclature of Complexes with Cationic and Anionic Coordination Spheres

There is also the possibility that a coordination compound is made of a complex cation and a complex anion. In this case, the rules discussed previously hold, the only new thing to learn is that we name the complex cation first and the complex anion second.

Exercise 2.3.5

Name this coordination compound.



Answer

In the compound, we have a diamminesilver (I) cation and a hexacyanoferrate (III) anion.

The name of the compound is diamminesilver (I) hexacyanoferrate (III).

Nomenclature of Complexes with Multiple Ligand Identities

What if there are different ligands in a coordination compound? In this case, we name the ligands in alphabetical order, and give each ligand a prefix according to its number.

Example 2.3.3

What is the name for this complex?

$[Co(NH_3)_4Cl_2]NO_3$

Solution

This is a compound with a complex cation containing ammine and chloro ligands. Because “a” comes before “c” in the alphabet we have to name the ammine ligand first. There are four ammine ligands and two chloro ligands. Therefore, we use the prefixes “tetra” in front of “ammine” and “di” in front of “chloro”. So the name starts “tetraamminedichloro”. Then, we name the metal which is cobalt. The oxidation number of cobalt is +3 because there are four charge-neutral ammine ligands, two anionic chloro ligands, and the charge at the complex cation is +1. +3 -2 = +1.

So the compound is called tetramminedichlorocobalt(III) nitrate.

Exercise 2.3.6

What is the name of this coordination compound?

$[Pt(NH_3)BrCl(H_2O)]SO_4$

Answer

In the compound $[Pt(NH_3)BrCl(H_2O)]SO_4$ there is a complex cation with four different ligands: an “ammine” ligand, a “bromo”-ligand, a "chloro"-ligand, and an "aqua" ligand. What is the order of them? According to the alphabet, “ammine” comes first, “aqua” is second, “bromo” is third, and “chloro” is fourth. They do not get a prefix because there is just one of them for each. The metal is platinum, and its oxidation state is +4 because the complex cation has a 2+ charge, and there are two neutral ligands, namely the aqua and the ammine ligands, and two anionic ones, namely the bromo and the chloro ligands: +4 - 2 = +2.

Therefore the compound's name is ammineaquabromochloroplatinum(IV) sulfate.

Nomenclature of Complexes with Complicated Ligands in a Coordination Sphere

So far we only considered relatively simple ligands that were either monoatomic, or contained a few atoms only. However, many ligands, in particular chelating ligands, contain more atoms, and have more complex names. These names may already contain prefixes that we use to number ligands. For example the ethylenediamine ligand is a chelating ligand with a longer name that already contains the prefix “di”. In such cases, to avoid ambiguity, we put the ligand name in parentheses, and place a somewhat different prefix in front of it to account for the number of the ligands.

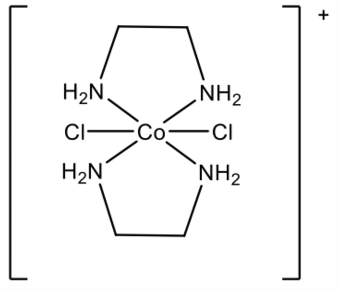
Table 2.3.3: Greek prefixes and prefixes for complicated ligands used for number of ligands in a coordination compound.

Number	2	3	4	5	6
Simple Prefix	di	tri	tetra	penta	hexa
Alternative Prefix	bis	tris	tetrakis	pentakis	hexakis

Instead of “di” we use “bis”, instead of “tri” we use “tris”, instead of “tetra” we use “tetrakis”, and so on (Table 2.3.3). When we use these alternative prefixes, the name of the ligand should always be included in parentheses.

✓ Example 2.3.4

What is the name of the complex cation shown here?



Solution

We first need to realize that there are two different ligands: chloro ligands and ethylenediamine ligands. We need to name the chloro ligands first, because they come first in the alphabet. Because there are two chloro ligands we use the prefix “di”. The ethylenediamine ligand is placed in parentheses, and the prefix “bis” is used instead of “di”. The metal is cobalt in the oxidation state +3 because the complex cation has a 1+ charge, and there are two chloro ligands with a 1- charge each, and two charge-neutral ethylenediamine ligands: +3 -2 = +1.

The name of the complex ion is dichlorobis(ethylenediamine)cobalt(III) ion.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

2.4: Geometries of Coordination Complexes

Coordination compounds adopt geometries around the central metal ion. These geometries can be predicted by valence bond theory. The most common structures of the complexes in coordination compounds are octahedral, tetrahedral, and square planar (Figure 2.4.1). For transition metal complexes, the coordination number determines the geometry around the central metal ion. Table 2.4.1 compares coordination numbers to the molecular geometry:

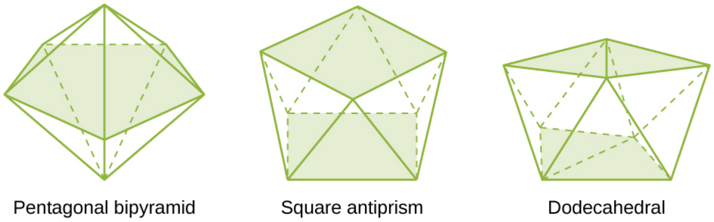


Figure 2.4.1: These are geometries of some complexes with coordination numbers of seven and eight.

Table 2.4.1: Coordination Numbers and Molecular Geometry

Coordination Number	**Molecular Geometry**	**Example**
2	linear	$[Ag(NH_3)_2]^+$
3	trigonal planar	$[Cu(CN)_3]^{2-}$
4	tetrahedral(d^0 or d^{10}), low oxidation states for M	$[Ni(CO)_4]$
4	square planar (d^8)	$[NiCl_4]^{2-}$
5	trigonal bipyramidal	$[CoCl_5]^{2-}$
5	square pyramidal	$[VO(CN)_4]^{2-}$
6	octahedral	$[CoCl_6]^{3-}$
7	pentagonal bipyramid	$[ZrF_7]^{3-}$
8	square antiprism	$[ReF_8]^{2-}$
8	dodecahedron	$[Mo(CN)_8]^{4-}$
9 and above	more complicated structures	$[ReH_9]^{2-}$

Unlike main group atoms in which both the bonding and nonbonding electrons determine the molecular shape, the nonbonding *d*-electrons do not change the arrangement of the ligands. Octahedral complexes have a coordination number of six, and the six donor atoms are arranged at the corners of an octahedron around the central metal ion. Examples are shown in Figure 2.4.2. The chloride and nitrate anions in $[Co(H_2O)_6]Cl_2$ and $[Cr(en)_3](NO_3)_3$, and the potassium cations in $K_2[PtCl_6]$, are outside the brackets and are not bonded to the metal ion.

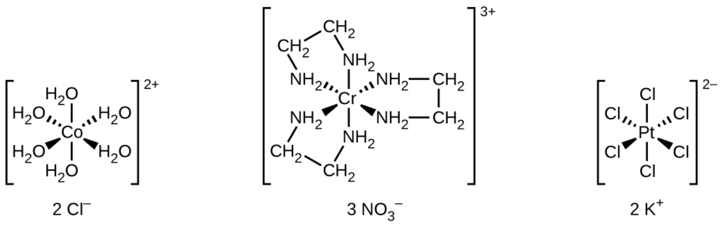


Figure 2.4.2: Many transition metal complexes adopt octahedral geometries, with six donor atoms forming bond angles of 90° about the central atom with adjacent ligands. Note that only ligands within the coordination sphere affect the geometry around the metal center.

For transition metals with a coordination number of four, two different geometries are possible: tetrahedral or square planar. Unlike main group elements, where these geometries can be predicted from VSEPR theory, a more detailed discussion of transition metal orbitals (discussed in the section on Crystal Field Theory) is required to predict which complexes will be tetrahedral and which will be square planar. In tetrahedral complexes such as $[Zn(CN)_4]^{2-}$ (Figure 2.4.3), each of the ligand pairs forms an angle of 109.5°. In square planar complexes, such as $[Pt(NH_3)_2Cl_2]$, each ligand has two other ligands at 90° angles (called the *cis* positions) and one additional ligand at an 180° angle, in the *trans* position.

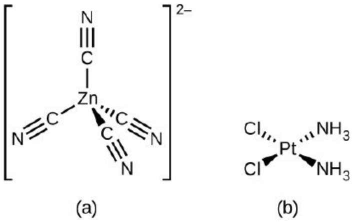


Figure 2.4.3: Transition metals with a coordination number of four can adopt a tetrahedral geometry (a) as in $K_2[Zn(CN)_4]$ or a square planar geometry (b) as shown in $[Pt(NH_3)_2Cl_2]$.

? Exercise 2.4.1

What are the geometries around each of the following complex ions?

a. $[Ni(H_2O)_6]Cl_2$

b. $K_3[Ag(S_2O_3)_2]$

c. $[Co(NH_3)_4Cl_2]NO_3$

Answer

a. The coordination number is 6, so the geometry is octahedral.

b. The coordination number is 2, so the geometry is linear.

c. The coordination number is 6, so the geometry is octahedral.

2.5: Isomerism

Here, we will apply isomerism to coordination chemistry. Some forms of isomerism in organic and coordination chemistry are the same, but there are some forms of isomerism that only occur in coordination chemistry.

Let us first briefly review the definition of isomerism: Isomerism is when two or more compounds have identical empirical formulas but different structures.

Definition: Isomerism

When two or more compounds have identical empirical formulas but different structures they are called isomers.

We distinguish between two basic types of isomerisms: constitutional isomerism and stereoisomerism. Remember, constitutional isomerism the bonds are not between the same atoms.

Definition: Constitutional Isomers

In constitutional isomers the bonds are not between the same atoms.

In stereoisomerism, the bonds are between the same atoms, but ligands are at different coordination sites.

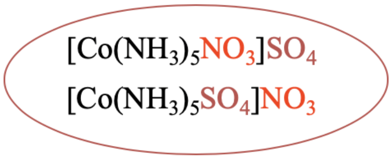
Definition: Stereoisomers

In stereoisomers, the bonds are between same atoms, but the ligands are at different coordination sites.

Forms of Constitutional Isomerism

Ionization Isomerism

One form of isomerism is the ionization isomerism. In this case one or more anionic ligand(s) and counterion(s) switch places.



$[Co(NH_3)_5NO_3]SO_4$

$[Co(NH_3)_5SO_4]NO_3$

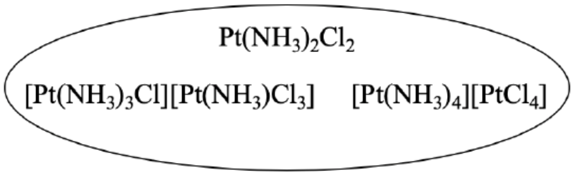
Figure 2.5.1. Two ionization isomers of the complex $[Co(NH_3)_5NO_3]SO_4$

For example, in the compound $[Co(NH_3)_5NO_3]SO_4$ there is a nitrate ion acting as a ligand, and a sulfate ion in acting as a counterion (Figure 2.5.1). There is an ionization isomer to this compound, in which the sulfate ion is now in the first coordination sphere, and the nitrate is in the second coordination sphere.

Coordination Isomerism

Another form of constitutional isomerism is coordination isomerism. In this isomerism, ligands are bound to different metal ions. Naturally, this implies that this form of isomerism can only exist if at least one isomer has two distinguishable metal ions.

For example, the compound $Pt(NH_3)_2Cl_2$ has two different coordination isomers. At first glance, they do not seem to be isomers at all. However, we can verify that they have the same empirical formula than the first compound (Figure 2.5.2).



$Pt(NH_3)_2Cl_2$

$[Pt(NH_3)_3Cl][Pt(NH_3)Cl_3]$ $[Pt(NH_3)_4][PtCl_4]$

Figure 2.5.2. Two different coordination isomers for the complex $Pt(NH_3)_2Cl_2$

$[Pt(NH_3)_3Cl][Pt(NH_3)Cl_3]$ has two Pt atoms, four NH_3 units and four Cl atoms. That makes $Pt_2(NH_3)_4Cl_4$. This formula can be divided by 2 to to give $Pt(NH_3)_2Cl_2$. We can now easily see that the two compounds are isomers. The third isomer also has two Pt atoms, four NH_3 units, and four chloro atoms, so it must be an isomer as well.

Linkage isomerism

Linkage isomerism, also called ambidentate isomerism, is an isomerism that can be observed for ligands that have more than one reactive end. In two linkage isomers, the ligands will bind with different ends to the metal.

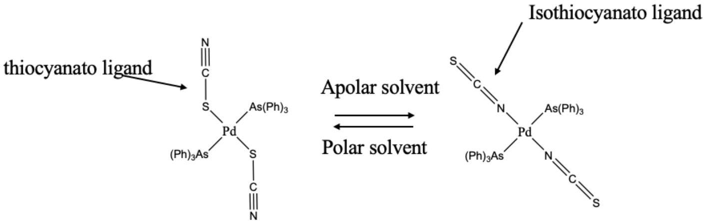


Figure 2.5.3. Two ambidentate isomers of thiocyanate

An example of an ambidentate ligand is the thiocyanate anion (Figure 2.5.3). It can bind either with the sulfur or with the nitrogen end to a metal ion. When it binds with the S-end it is called the thiocyanato ligand, when it binds with the N-end it is called the isothiocyanato ligand. Which atom binds to the metal can depend on the solvent. It is even possible that two, same ambidentate ligands bind with opposite ends to the metal in one and the same molecule. An example is the complex shown (Figure 2.5.4). In this molecule, there is a thiocyanato and an isocyanato ligand binding to Pd.

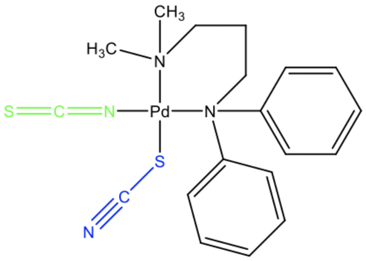


Figure 2.5.4. An example of two, same ambidentate ligands binding with opposite ends to the metal in one and the same molecule.

Thio- and isothiocyanato ligands are not the only examples of ambidentate ligands.

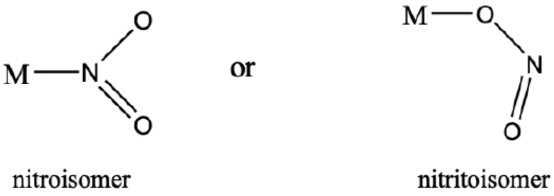


Figure 2.5.5. Two linkage isomers of the nitrite anion

Another example is the nitrite anion. It can either bind with the N- end or the O-end to a metal. In the first case it is called a nitroisomer, in the latter it is called a nitrito isomer (Figure 2.5.5). Nitritoisomers are usually more stable.

Stereoisomers (Configuration Isomers)

Now let us discuss the second major type of isomerism: stereisomerism. As mentioned previously, in stereoisomerism the bonds are between the same atoms, but the positions at which the ligands bind, the coordination sites, are different. There are two basic types of stereoisomerism: diastereomerism and enantiomerism (Figure 2.5.6).

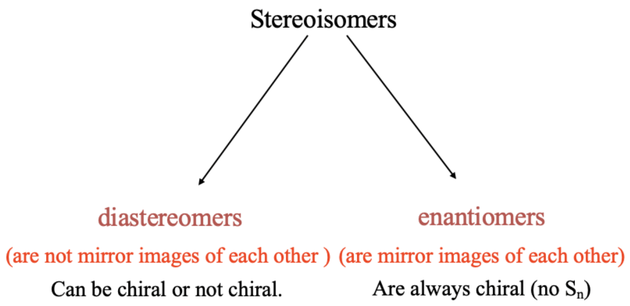


Figure 2.5.6. Types of stereoisomerism

In diastereomerism, the diastereomers are not mirror images to each other.

Definition: Diastereomers

Diastereomers are stereoisomers that are not mirror images of each other. They can be chiral or not chiral.

In enantiomerism, the enantiomers are mirror images to each others. Enantiomers are always chiral molecules.

Definition: Enantiomers

Stereoisomers that are mirror images of each other. They are always chiral.

Diastereomers can be chiral, but do not have to be chiral. Remember, a molecule is chiral when it does not contain an internal plane of symmetry.

Cis-Trans Isomerism

Let us now discuss some common forms of stereoisomerism. The cis-trans isomerism is one very common stereoisomerism. It occurs when two, same ligands are in adjacent or opposite positions. For example, in a square planar complex two ligands can be adjacent or in opposite positions. When in adjacent position, the bond angle is 90° and we have a cis-isomer, when in opposite position, the bond angle is 180° and we have a trans-isomer.

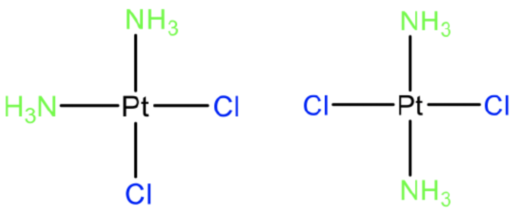


Figure 2.5.7 Cis-platinum and trans-platinum, respectively

The probably most well known example of a cis-isomer in coordination chemistry is cis-platinum which is an anti-cancer drug (Figure 2.5.7). Its trans-isomers does not have these pharmaceutical properties showing that cis-trans isomerism can have a profound impact on the properties of a molecule. Overall cis-trans isomerism in Pt(II) complexes have been most intensely studied, but cis-trans isomerism is also known for other d^8 metal ions in square planar complexes. We can also ask if cis- and trans isomers are diastereomers or enantiomers. Let us look at the example of cis- and trans-platinum to answer this question. Clearly, these two isomers are not mirror images to each other, so they must be diasteromers. Generally, cis- and trans- isomers are diastereomers.

Cis-trans isomerism extends beyond square planar complexes, and is also known for other shapes, for example, the octahedral shape. In the cis-isomer of an octahedral complex two ligands occupy positions on the same face of the octahedron, whereas in the trans-isomer they occupy opposite position of the octahedron.

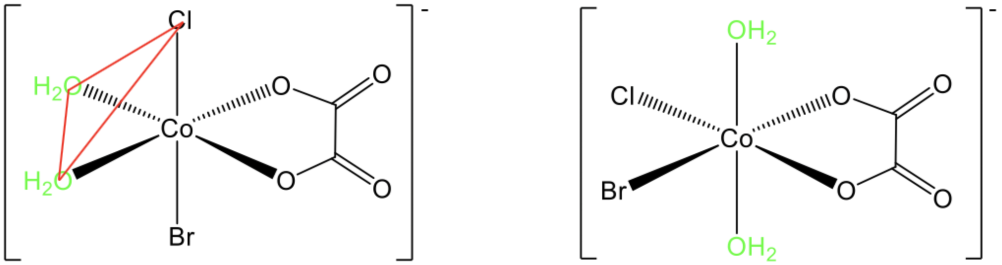


Figure 2.5.8. Cis and trans isomers of the diaquabromochlorooxalato cobalt(1-) complex, respectively

For example, in the complex diaquabromochlorooxalato cobalt(1-) there are cis and trans isomers known (Figure 2.5.8). In the trans-isomer the two aqua-ligands stand in opposite position, and there is a 180° angle between them. In the cis-isomer they are in adjacent position, and the angle is 90°. We can see that the two ligands are on the same triangular face of the octahedron, shown in red.

Fac-mer Isomerism

Another common type of stereoisomerism in coordination chemistry is fac-mer isomerism. Fac stands for facial and mer stands for meridional. In a fac-isomer the same ligands are on a common face of a polyhedral complex, in the mer isomer they are on a plane that bisects the polyhedron. This kind of isomerism is very common for octahedral complexes, but not restricted to those.

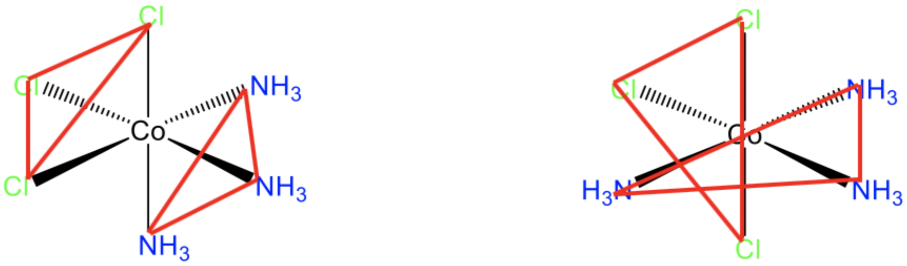


Figure 2.5.9. Fac- (left) and mer-isomers (right) of the triammine trichloro cobalt(III) complex.

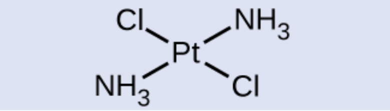
For example the complex triamminetrichlorocobalt(III) has a fac- and a mer-isomer. You can see that in the fac-isomer the identical ligands are on two opposite triangular faces of the octahedron. In the mer-isomers they lie on two planes that bisect the octahedron. We can again ask if they are diastereomers or enantiomers? The answer is: They are not mirror images to each other, so they are not enantiomers, but diastereomers.

✓ Example 2.5.1: Geometric Isomers

Identify which geometric isomer of [$Pt(NH_3)_2Cl_2$] is shown in Figure 2.5.9b. Draw the other geometric isomer and give its full name.

Solution

In the Figure 2.5.9b, the two chlorine ligands occupy *cis* positions. The other form is shown in below. When naming specific isomers, the descriptor is listed in front of the name. Therefore, this complex is *trans*-diaminedichloroplatinum(II).

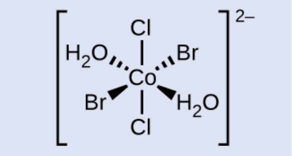


The *trans* isomer of [$Pt(NH_3)_2Cl_2$] has each ligand directly across from an adjacent ligand.

? Exercise 2.5.1

Draw the ion *trans*-diaqua-*trans*-dibromo-*trans*-dichlorocobalt(II).

Answer



Optical Isomerism

Another important type of isomers are optical isomers, or enantiomers, in which two objects are exact mirror images of each other but cannot be lined up so that all parts match. This means that optical isomers are nonsuperimposable mirror images. A classic example of this is a pair of hands, in which the right and left hand are mirror images of one another but cannot be superimposed. Optical isomers are very important in organic and biochemistry because living systems often incorporate one specific optical isomer and not the other. Unlike geometric isomers, pairs of optical isomers have identical properties (boiling point, polarity, solubility, etc.). Optical isomers differ only in the way they affect polarized light and how they react with other optical isomers. For coordination complexes, many coordination compounds such as $[M(en)_3]^{n+}$ [in which M^{n+} is a central metal ion such as iron(III) or cobalt(II)] form enantiomers, as shown in Figure 2.5.10. These two isomers will react differently with other optical isomers. For example, DNA helices are optical isomers, and the form that occurs in nature (right-handed DNA) will bind to only one isomer of $[M(en)_3]^{n+}$ and not the other.

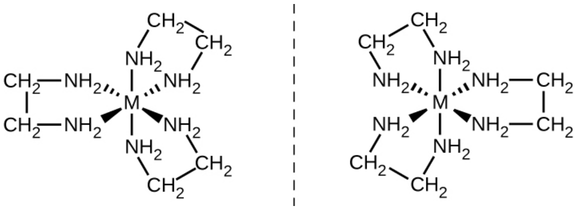


Figure 2.5.10: The complex $[M(en)_3]^{n+}$ (M^{n+} = a metal ion, en = ethylenediamine) has a nonsuperimposable mirror image.

The $[Co(en)_2Cl_2]^+$ ion exhibits geometric isomerism (*cis*/*trans*), and its *cis* isomer exists as a pair of optical isomers (Figure 2.5.11).

For the cis isomers, the structural formula shown are mirror images of one another. The two chlorine atoms are adjacent to one another in each cis structure. The trans form is also shown with the chlorine directly opposite from one another.

Figure 2.5.11: Three isomeric forms of $[Co(en)_2Cl_2]^+$ exist. The trans isomer, formed when the chlorines are positioned at a 180° angle, has very different properties from the cis isomers. The mirror images of the cis isomer form a pair of optical isomers, which have identical behavior except when reacting with other enantiomers.

Glossary

***cis* configuration**

configuration of a geometrical isomer in which two similar groups are on the same side of an imaginary reference line on the molecule

ionization isomer

(or coordination isomer) isomer in which an anionic ligand is replaced by the counter ion in the inner coordination sphere

linkage isomer

coordination compound that possesses a ligand that can bind to the transition metal in two different ways (CN^- vs. NC^-)

optical isomer

(also, enantiomer) molecule that is a nonsuperimposable mirror image with identical chemical and physical properties, except when it reacts with other optical isomers

***trans* configuration**

configuration of a geometrical isomer in which two similar groups are on opposite sides of an imaginary reference line on the molecule

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

2.6: Optical and Magnetic Properties of Coordination Compounds

Learning Objectives

- Outline the basic premise of crystal field theory (CFT)
- Identify molecular geometries associated with various d-orbital splitting patterns
- Predict electron configurations of split d orbitals for selected transition metal atoms or ions
- Explain spectral and magnetic properties in terms of CFT concepts

The behavior of coordination compounds cannot be adequately explained by the same theories used for main group element chemistry. The observed geometries of coordination complexes are not consistent with hybridized orbitals on the central metal overlapping with ligand orbitals, as would be predicted by valence bond theory. The observed colors indicate that the *d* orbitals often occur at different energy levels rather than all being degenerate, that is, of equal energy, as are the three *p* orbitals. To explain the stabilities, structures, colors, and magnetic properties of transition metal complexes, a different bonding model has been developed. Just as valence bond theory explains many aspects of bonding in main group chemistry, crystal field theory is useful in understanding and predicting the behavior of transition metal complexes.

2.6.1: Crystal Field Theory

To explain the observed behavior of transition metal complexes (such as how colors arise), a model involving electrostatic interactions between the electrons from the ligands and the electrons in the unhybridized *d* orbitals of the central metal atom has been developed. This electrostatic model is crystal field theory (CFT). It allows us to understand, interpret, and predict the colors, magnetic behavior, and some structures of coordination compounds of transition metals.

CFT focuses on the nonbonding electrons on the central metal ion in coordination complexes not on the metal-ligand bonds. Like valence bond theory, CFT tells only part of the story of the behavior of complexes. However, it tells the part that valence bond theory does not. In its pure form, CFT ignores any covalent bonding between ligands and metal ions. Both the ligand and the metal are treated as infinitesimally small point charges.

All electrons are negative, so the electrons donated from the ligands will repel the electrons of the central metal. Let us consider the behavior of the electrons in the unhybridized *d* orbitals in an octahedral complex. The five *d* orbitals consist of lobe-shaped regions and are arranged in space, as shown in Figure $2.6.1$. In an octahedral complex, the six ligands coordinate along the axes.

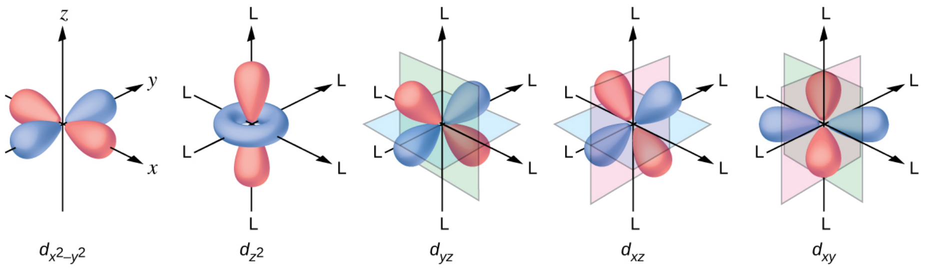


Figure 2.6.1: The directional characteristics of the five d orbitals are shown here. The shaded portions indicate the phase of the orbitals. The ligands (L) coordinate along the axes. For clarity, the ligands have been omitted from the $d_{x^2-y^2}$ *orbital so that the axis labels could be shown.*

This figure includes diagrams of five d orbitals. Each diagram includes three axes. The z-axis is vertical and is denoted with an upward pointing arrow. It is labeled “z” in the first diagram. Arrows similarly identify the x-axis with an arrow pointing from the rear left to the right front, diagonally across the figure and the y-axis with an arrow pointing from the left front diagonally across the figure to the right rear of the diagram. These axes are similarly labeled as “x” and “y.” In this first diagram, four orange balloon-like shapes extend from a point at the origin out along the x- and y- axes in positive and negative directions covering just over half the length of the positive and negative x- and y- axes. Beneath the diagram is the label, “d subscript (x superscript 2 minus y superscript 2).” The second diagram just right of the first is similar except the x, y, and z labels have been replaced in each instance with the letter L. Only a pair of the orange balloon-like shapes are present and extend from the origin above and below along the vertical axis. An orange toroidal or donut shape is positioned around the origin, oriented through the x- and y- axes. This shape extends out to about a third of the length of the positive and negative regions of the x- and y- axes. This diagram is labeled, “d subscript (z superscript 2).” The third through fifth diagrams, similar to the first, show four orange balloon-like shapes. These diagrams differ however in the orientation of the shapes along the axes and the x-, y-, and z-axis labels have each been replaced with the letter L. Planes are added to the figures to help show the orientation differences with these diagrams. In the third diagram, a green plane is oriented vertically through the length of the x-axis and a blue plane is oriented horizontally through the length of the y-axis. The balloon shapes extend from the origin to the spaces between the positive z- and negative y- axes, positive z- and positive y- axes, negative z- and negative y- axes, and negative z- and positive y- axes. This diagram is labeled, “d subscript (y z).” In the fourth diagram, a green plane is oriented vertically through the x- and y- axes and a blue plane is oriented horizontally through the length of the x-axis. The balloon shapes extend from the origin to the spaces between the positive z- and negative x- axes, positive z- and positive x- axes, negative z- and negative x- axes, and negative z- and positive x- axes. This diagram is labeled “d subscript (x z).” In the fifth diagram, a pink plane is oriented vertically through the length of the y-axis and a green plane is oriented vertically through the length of the x-axis. The balloon shapes extend from the origin to the spaces between the positive x- and negative y- axes, positive x- and positive y- axes, negative x- and negative y- axes, and negative x- and positive y- axes. This diagram is labeled, “d subscript (x y).”

In an uncomplexed metal ion in the gas phase, the electrons are distributed among the five *d* orbitals in accord with Hund's rule because the orbitals all have the same energy. However, when ligands coordinate to a metal ion, the energies of the *d* orbitals are no longer the same.

In octahedral complexes, the lobes in two of the five *d* orbitals, the d_{z^2} and $d_{x^2-y^2}$ orbitals, point toward the ligands (Figure 2.6.1). These two orbitals are called the e_g orbitals (the symbol actually refers to the symmetry of the orbitals, but we will use it as a convenient name for these two orbitals in an octahedral complex). The other three orbitals, the d_{xy}, d_{xz}, and d_{yz} orbitals, have lobes that point between the ligands and are called the t_{2g} orbitals (again, the symbol really refers to the symmetry of the orbitals). As six ligands approach the metal ion along the axes of the octahedron, their point charges repel the electrons in the *d* orbitals of the metal ion. However, the repulsions between the electrons in the e_g orbitals (the d_{z^2} and $d_{x^2-y^2}$ orbitals) and the ligands are greater than the repulsions between the electrons in the t_{2g} orbitals (the d_{zy}, d_{xz}, and d_{yz} orbitals) and the ligands. This is because the lobes of the e_g orbitals point directly at the ligands, whereas the lobes of the t_{2g} orbitals point between them. Thus, electrons in the e_g orbitals of the metal ion in an octahedral complex have higher potential energies than those of electrons in the t_{2g} orbitals. The difference in energy may be represented as shown in Figure 2.6.2.

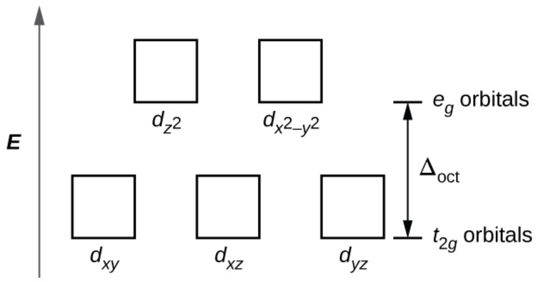


Figure 2.6.2: In octahedral complexes, the e_g orbitals are destabilized (higher in energy) compared to the t_{2g} orbitals because the ligands interact more strongly with the d orbitals at which they are pointed directly.

The difference in energy between the e_g and the t_{2g} orbitals is called the crystal field splitting and is symbolized by Δoct, where oct stands for octahedral.

The magnitude of Δ_{oct} depends on many factors, including the nature of the six ligands located around the central metal ion, the charge on the metal, and whether the metal is using 3*d*, 4*d*, or 5*d* orbitals. Different ligands produce different crystal field splittings. The increasing crystal field splitting produced by ligands is expressed in the spectrochemical series, a short version of which is given here:

$$\xrightarrow[\text{a few ligands of the spectrochemical series, in order of increasing field strength of the ligand}]{\mathrm{I^-} < \mathrm{Br^-} < \mathrm{Cl^-} < \mathrm{F^-} < \mathrm{H_2O} < \mathrm{C_2O_4^{2-}} < \mathrm{NH_3} < en < \mathrm{NO_2^-} < \mathrm{CN^-}}$$

In this series, ligands on the left cause small crystal field splittings and are weak-field ligands, whereas those on the right cause larger splittings and are strong-field ligands. Thus, the Δ_{oct} value for an octahedral complex with iodide ligands (I^-) is much smaller than the Δ_{oct} value for the same metal with cyanide ligands (CN^-).

Electrons in the *d* orbitals follow the aufbau (“filling up”) principle, which says that the orbitals will be filled to give the lowest total energy, just as in main group chemistry. When two electrons occupy the same orbital, the like charges repel each other. The energy needed to pair up two electrons in a single orbital is called the pairing energy (P). Electrons will always singly occupy each orbital in a degenerate set before pairing. P is similar in magnitude to Δ_{oct}. When electrons fill the *d* orbitals, the relative magnitudes of Δ_{oct} and P determine which orbitals will be occupied.

In $[Fe(CN)_6]^{4-}$, the strong field of six cyanide ligands produces a large Δ_{oct}. Under these conditions, the electrons require less energy to pair than they require to be excited to the e_g orbitals ($\Delta_{oct} > P$). The six 3*d* electrons of the Fe^{2+} ion pair in the three t_{2g} orbitals (Figure 2.6.3). Complexes in which the electrons are paired because of the large crystal field splitting are called low-spin complexes because the number of unpaired electrons (spins) is minimized.

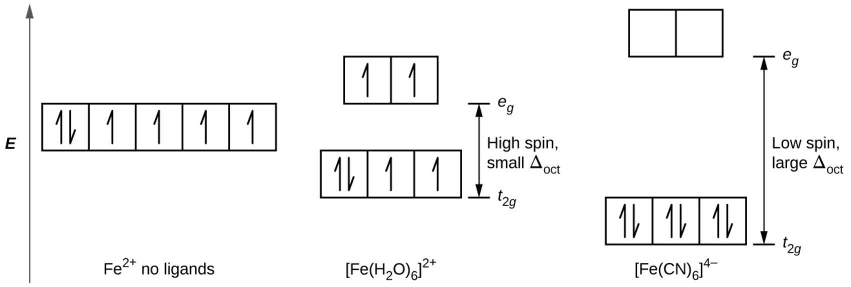


Figure 2.6.3: Iron(II) complexes have six electrons in the 5d orbitals. In the absence of a crystal field, the orbitals are degenerate. For coordination complexes with strong-field ligands such as $[Fe(CN)_6]^{4-}$, Δ_{oct} is greater than P, and the electrons pair in the lower energy t_{2g} orbitals before occupying the eg orbitals. With weak-field ligands such as H_2O, the ligand field splitting is less than the pairing energy, Δ_{oct} less than P, so the electrons occupy all d orbitals singly before any pairing occurs.

In $[Fe(H_2O)_6]^{2+}$, on the other hand, the weak field of the water molecules produces only a small crystal field splitting ($\Delta_{oct} < P$). Because it requires less energy for the electrons to occupy the e_g orbitals than to pair together, there will be an electron in each of the five 3*d* orbitals before pairing occurs. For the six *d* electrons on the iron(II) center in $[Fe(H_2O)_6]^{2+}$, there will be one pair of electrons and four unpaired electrons (Figure 2.6.3). Complexes such as the $[Fe(H_2O)_6]^{2+}$ ion, in which the electrons are unpaired because the crystal field splitting is not large enough to cause them to pair, are called high-spin complexes because the number of unpaired electrons (spins) is maximized.

A similar line of reasoning shows why the $[Fe(CN)_6]^{3-}$ ion is a low-spin complex with only one unpaired electron, whereas both the $[Fe(H_2O)_6]^{3+}$ and $[FeF_6]^{3-}$ ions are high-spin complexes with five unpaired electrons.

✓ Example 2.6.1: High- and Low-Spin Complexes

Predict the number of unpaired electrons.

a. $K_3[CrI_6]$
b. $[Cu(en)_2(H_2O)_2]Cl_2$
c. $Na_3[Co(NO_2)_6]$

Solution

The complexes are octahedral.

a. Cr^{3+} has a d^3 configuration. These electrons will all be unpaired.
b. Cu^{2+} is d^9, so there will be one unpaired electron.
c. Co^{3+} has d^6 valence electrons, so the crystal field splitting will determine how many are paired. Nitrite is a strong-field ligand, so the complex will be low spin. Six electrons will go in the t_{2g} orbitals, leaving 0 unpaired.

? Exercise 2.6.1

The size of the crystal field splitting only influences the arrangement of electrons when there is a choice between pairing electrons and filling the higher-energy orbitals. For which d-electron configurations will there be a difference between high- and low-spin configurations in octahedral complexes?

Answer

d^4, d^5, d^6, and d^7

✓ Example 2.6.2: CFT for Other Geometries

CFT is applicable to molecules in geometries other than octahedral. In octahedral complexes, remember that the lobes of the e_g set point directly at the ligands. For tetrahedral complexes, the d orbitals remain in place, but now we have only four ligands located between the axes (Figure 2.6.4). None of the orbitals points directly at the tetrahedral ligands. However, the e_g set (along the Cartesian axes) overlaps with the ligands less than does the t_{2g} set. By analogy with the octahedral case, predict the energy diagram for the d orbitals in a tetrahedral crystal field. To avoid confusion, the octahedral e_g set becomes a tetrahedral e set, and the octahedral t_{2g} set becomes a t_2 set.

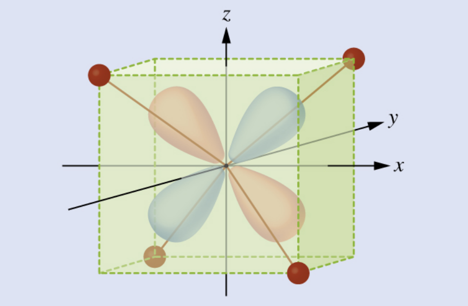
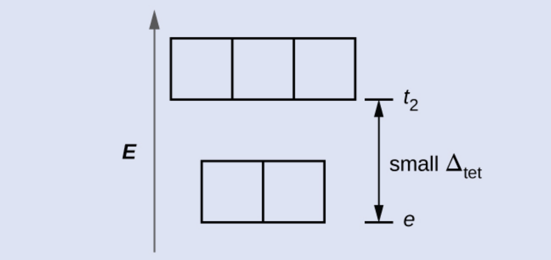


Figure 2.6.4: This diagram shows the orientation of the tetrahedral ligands with respect to the axis system for the orbitals.

Solution

Since CFT is based on electrostatic repulsion, the orbitals closer to the ligands will be destabilized and raised in energy relative to the other set of orbitals. The splitting is less than for octahedral complexes because the overlap is less, so Δ_{tet} is usually small $\left(\Delta_{tet} = \frac{4}{9}\Delta_{oct}\right)$:



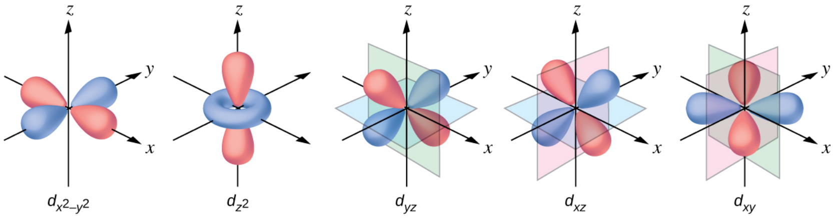
Exercise 2.6.2

Explain how many unpaired electrons a tetrahedral d^4 ion will have.

Answer

4; because Δ_{tet} is small, all tetrahedral complexes are high spin and the electrons go into the t_2 orbitals before pairing

The other common geometry is square planar. It is possible to consider a square planar geometry as an octahedral structure with a pair of *trans* ligands removed. The removed ligands are assumed to be on the *z*-axis. This changes the distribution of the *d* orbitals, as orbitals on or near the *z*-axis become more stable, and those on or near the *x*- or *y*-axes become less stable. This results in the octahedral t_{2g} and the e_g sets splitting and gives a more complicated pattern with no simple Δ_{oct}. The basic pattern is:



2.6.2: Magnetic Moments of Molecules and Ions

Experimental evidence of magnetic measurements supports the theory of high- and low-spin complexes. Remember that molecules such as O_2 that contain unpaired electrons are paramagnetic. Paramagnetic substances are attracted to magnetic fields. Many transition metal complexes have unpaired electrons and hence are paramagnetic. Molecules such as N_2 and ions such as Na^+ and $[Fe(CN)_6]^{4-}$ that contain no unpaired electrons are diamagnetic. Diamagnetic substances have a slight tendency to be repelled by magnetic fields.

When an electron in an atom or ion is unpaired, the magnetic moment due to its spin makes the entire atom or ion paramagnetic. The size of the magnetic moment of a system containing unpaired electrons is related directly to the number of such electrons: the greater the number of unpaired electrons, the larger the magnetic moment. Therefore, the observed magnetic moment is used to determine the number of unpaired electrons present. The measured magnetic moment of low-spin d^6 $[Fe(CN)_6]^{4-}$ confirms that iron is diamagnetic, whereas high-spin d^6 $[Fe(H_2O)_6]^{2+}$ has four unpaired electrons with a magnetic moment that confirms this arrangement.

2.6.3: Colors of Transition Metal Complexes

When atoms or molecules absorb light at the proper frequency, their electrons are excited to higher-energy orbitals. For many main group atoms and molecules, the absorbed photons are in the ultraviolet range of the electromagnetic spectrum, which cannot be detected by the human eye. For coordination compounds, the energy difference between the *d* orbitals often allows photons in the visible range to be absorbed.

The human eye perceives a mixture of all the colors, in the proportions present in sunlight, as white light. Complementary colors, those located across from each other on a color wheel, are also used in color vision. The eye perceives a mixture of two complementary colors, in the proper proportions, as white light. Likewise, when a color is missing from white light, the eye sees its complement. For example, when red photons are absorbed from white light, the eyes see the color green. When violet photons are removed from white light, the eyes see lemon yellow. The blue color of the $[Cu(NH_3)_4]^{2+}$ ion results because this ion absorbs orange and red light, leaving the complementary colors of blue and green (Figure 2.6.5).

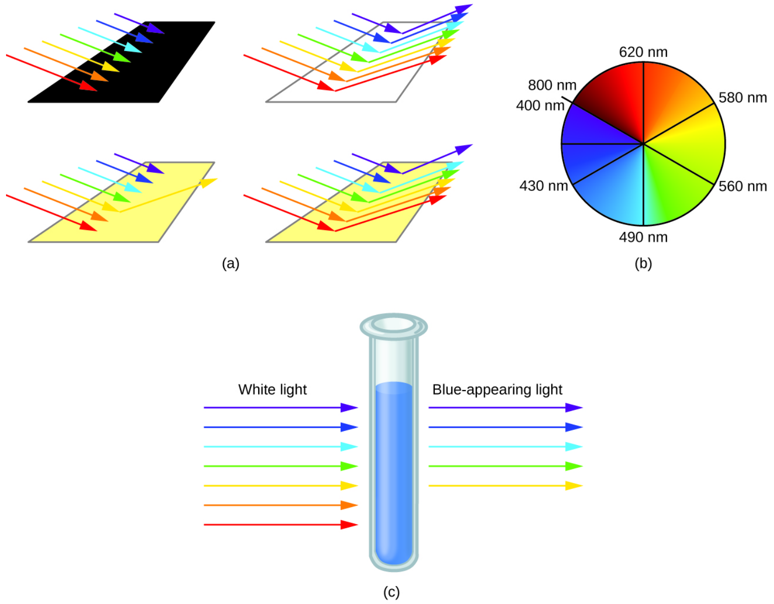


Figure 2.6.5: (a) An object is black if it absorbs all colors of light. If it reflects all colors of light, it is white. An object has a color if it absorbs all colors except one, such as this yellow strip. The strip also appears yellow if it absorbs the complementary color from white light (in this case, indigo). (b) Complementary colors are located directly across from one another on the color wheel. (c) A solution of $[Cu(NH_3)_4]^{2+}$ ions absorbs red and orange light, so the transmitted light appears as the complementary color, blue.

✓ Example 2.6.3: Colors of Complexes

The octahedral complex $[Ti(H_2O)_6]^{3+}$ has a single *d* electron. To excite this electron from the ground state t_{2g} orbital to the e_g orbital, this complex absorbs light from 450 to 600 nm. The maximum absorbance corresponds to Δ_{oct} and occurs at 499 nm. Calculate the value of Δ_{oct} in Joules and predict what color the solution will appear.

Solution

Using Planck's equation (refer to the section on electromagnetic energy), we calculate:

$$v = \frac{c}{\lambda} \text{ so } \frac{3.00\times10^{8}\text{ m/s}}{\frac{499\text{ nm}\times1\text{ m}}{10^{9}\text{ nm}}} = 6.01\times10^{14}\text{ Hz}$$

$$E = hnu \text{ so } 6.63\times10^{-34}\text{ J}\cdot\text{s}\times6.01\times10^{14}\text{ Hz} = 3.99\times10^{-19}\text{ Joules/ion}$$

Because the complex absorbs 600 nm (orange) through 450 (blue), the indigo, violet, and red wavelengths will be transmitted, and the complex will appear purple.

? Exercise 2.6.3

A complex that appears green, absorbs photons of what wavelengths?

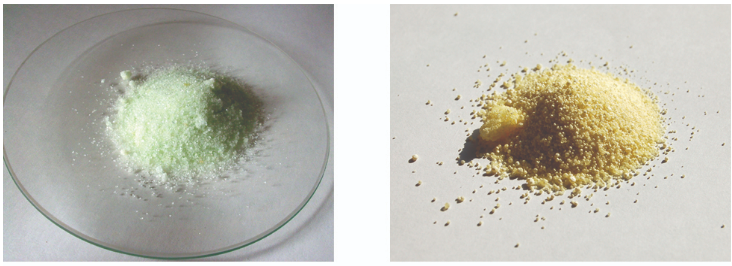
Answer

red, 620–800 nm

Small changes in the relative energies of the orbitals that electrons are transitioning between can lead to drastic shifts in the color of light absorbed. Therefore, the colors of coordination compounds depend on many factors. As shown in Figure 2.6.6, different aqueous metal ions can have different colors. In addition, different oxidation states of one metal can produce different colors, as shown for the vanadium complexes in the link below.

Figure 2.6.6: The partially filled d orbitals of the stable ions $Cr^{3+}(aq)$, $Fe^{3+}(aq)$, and $Co^{2+}(aq)$ (left, center and right, respectively) give rise to various colors. (credit: Sahar Atwa)

The specific ligands coordinated to the metal center also influence the color of coordination complexes. For example, the iron(II) complex $[Fe(H_2O)_6]SO_4$ appears blue-green because the high-spin complex absorbs photons in the red wavelengths (Figure 2.6.7). In contrast, the low-spin iron(II) complex $K_4[Fe(CN)_6]$ appears pale yellow because it absorbs higher-energy violet photons.



(a) (b)

Figure 2.6.7: Both (a) hexaaquairon(II) sulfate and (b) potassium hexacyanoferrate(II) contain d^6 iron(II) octahedral metal centers, but they absorb photons in different ranges of the visible spectrum.

In general, strong-field ligands cause a large split in the energies of *d* orbitals of the central metal atom (large Δ_{oct}). Transition metal coordination compounds with these ligands are yellow, orange, or red because they absorb higher-energy violet or blue light. On the other hand, coordination compounds of transition metals with weak-field ligands are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.

Video 2.6.8: Watch this video of the reduction of vanadium complexes to observe the colorful effect of changing oxidation states.

A coordination compound of the Cu^+ ion has a d^{10} configuration, and all the e_g orbitals are filled. To excite an electron to a higher level, such as the 4*p* orbital, photons of very high energy are necessary. This energy corresponds to very short wavelengths in the ultraviolet region of the spectrum. No visible light is absorbed, so the eye sees no change, and the compound appears white or colorless. A solution containing $[Cu(CN)_2]^-$, for example, is colorless. On the other hand, octahedral Cu^{2+} complexes have a vacancy in the e_g orbitals, and electrons can be excited to this level. The wavelength (energy) of the light absorbed corresponds to the visible part of the spectrum, and Cu^{2+} complexes are almost always colored—blue, blue-green violet, or yellow (Figure 2.6.8).

Although CFT successfully describes many properties of coordination complexes, molecular orbital explanations (beyond the introductory scope provided here) are required to understand fully the behavior of coordination complexes.

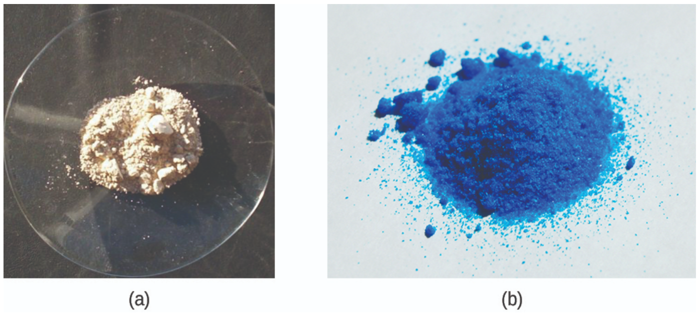

(a) (b)

Figure 2.6.8: (a) Copper(I) complexes with d^{10} configurations such as CuI tend to be colorless, whereas (b) d^9 copper(II) complexes such as $Cu(NO_3)_2 \cdot 5H_2O$ are brightly colored.

Summary

Crystal field theory treats interactions between the electrons on the metal and the ligands as a simple electrostatic effect. The presence of the ligands near the metal ion changes the energies of the metal *d* orbitals relative to their energies in the free ion. Both the color and the magnetic properties of a complex can be attributed to this crystal field splitting. The magnitude of the splitting (Δ_{oct}) depends on the nature of the ligands bonded to the metal. Strong-field ligands produce large splitting and favor low-spin complexes, in which the t_{2g} orbitals are completely filled before any electrons occupy the e_g orbitals. Weak-field ligands favor formation of high-spin complexes. The t_{2g} and the e_g orbitals are singly occupied before any are doubly occupied.

Glossary

crystal field splitting (Δ_{oct})

difference in energy between the t_{2g} and e_g sets or *t* and *e* sets of orbitals

crystal field theory

model that explains the energies of the orbitals in transition metals in terms of electrostatic interactions with the ligands but does not include metal ligand bonding

e_g orbitals

set of two *d* orbitals that are oriented on the Cartesian axes for coordination complexes; in octahedral complexes, they are higher in energy than the t_{2g} orbitals

geometric isomers

isomers that differ in the way in which atoms are oriented in space relative to each other, leading to different physical and chemical properties

high-spin complex

complex in which the electrons maximize the total electron spin by singly populating all of the orbitals before pairing two electrons into the lower-energy orbitals

low-spin complex

complex in which the electrons minimize the total electron spin by pairing in the lower-energy orbitals before populating the higher-energy orbitals

pairing energy (P)

energy required to place two electrons with opposite spins into a single orbital

spectrochemical series

ranking of ligands according to the magnitude of the crystal field splitting they induce

strong-field ligand

ligand that causes larger crystal field splittings

t_{2g} orbitals

set of three *d* orbitals aligned between the Cartesian axes for coordination complexes; in octahedral complexes, they are lowered in energy compared to the e_g orbitals according to CFT

weak-field ligand

ligand that causes small crystal field splittings

2.7: Transition Metals and Coordination Chemistry (Exercises)

1. Write the electron configurations for each of the following elements:

a. Sc

Let's start off by identifying where Scandium sits on the periodic table: row 4, group 3. This identification is the critical basis we need to write its electron configuration.

By looking at Scandium's atomic number, 21, it gives us both the number of protons and the number of electrons. At the end of writing its electron configuration, the electrons should add up to 21.

At row 4, group 3 Sc, is a transition metal; meaning that its electron configuration will include the D orbital.

Now, we can begin to assign the 21 electrons of Sc to orbitals. As you assign electrons to their orbitals, you move right across the periodic table.

Its first 2 electrons are in the 1s orbital which is denoted as

$1s^2$

where the "1" preceding the s denotes the fact that it is of row one, and it has an exponent of 2 because it fulfills the s orbital's maximum electron number. Now we have 21-2=19 more electrons to assign.

Its next 2 electrons are in the 2s orbital which is denoted as

$2s^2$

where the "2" preceding the s indicates that it is of row two, and it has an exponent of 2 because it fulfills the s orbital's maximum electron number. Now we have 19-2=17 more electrons to assign.

Its next 6 electrons are in the 2p orbital which is denoted as

$2p^6$

where the "2" preceding the p indicates that it is of row two, and it has an exponent of 6 because it fulfills the p orbital's maximum electron number. Now we have 17-6=11 more electrons to assign.

Its next 2 electrons are in the 3s orbital which is denoted as

$3s^2$

where the "3" preceding the s indicates that it is of row three, and it has an exponent of 2 because it fulfills the s orbital's maximum electron number. Now we have 11-2=9 more electrons to assign.

Its next 6 electrons are in the 3p orbital which is denoted as

$3p^6$

where the "3" preceding the p indicates that it is of row three, and it has an exponent of 6 because it fulfills the p orbital's maximum electron number. Now we have 9-6=3 more electrons to assign.

Its next 2 electrons are in the 4s orbital which is denoted as

$4s^2$

where the "4" preceding the s indicates that it is of row four, and it has an exponent of 2 because it fulfills the s orbital's maximum electron number. Now we have 3-2=1 more electron to assign.

Its last electron would be alone in the 3 d orbital which is denoted as

$3d^1$

where the "3" preceding the d indicates that, even though it is technically of row 4, by disregarding the first row of H and He, this is the third row and it has an exponent of 1 because there is only 1 electron to be placed in the d orbital. Now we have assigned all of the electrons to the appropriate orbitals and sub-orbitals, so that the final, entire electron configuration is written as:

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

This is the long-hand version of its electron configuration.

So for Sc, its short-hand version of its electron configuration would therefore be:

$[Ar]\ 4s^2 3d^1$

b. Ti

Start off by identifying where Titanium sits on the periodic table: row 4, group 4, meaning it has 22 electrons total. Titanium is one element to the right of the previous problem's Sc, so we will basically use the same method except, in the end, there will be 2 electrons remaining, so therefore the final orbital will be denoted as:

$3d^2$

If needed, look above to the exact steps for how to do it in detail again; the long-hand electron configuration for Titanium will be:

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

> So for Ti, its short-hand version of its electron configuration would therefore be:
>
> $[Ar]\ 4s^23d^2$

c. Cr

c. Cr

Start off by identifying where Chromium sits on the periodic table: row 4, group 6, that means it has a total of 24 electrons. But first, Cr, along with Mo, Nb, Ru, Rh, Pd, Cu, Sg, Pt and Au, is a special case. You would think that since it has 24 electrons that its configuration would look like:

$1s^22s^22p^63s^23p^64s^23d^4$

> which is how we learned it earlier. However, this electron configuration is very unstable because of the fact that there are 4 electrons in its 3 d orbital. The most stable configurations are half-filled (d^5) and full orbitals (d^{10}), so the elements with electrons resulting in ending with the d^4 or d^9 are so unstable that we write its stable form instead, where an electron from the preceding s orbital will be moved to fill the d orbital, resulting in a stable orbital.

If needed, look above to the exact steps for how to do the beginning of the configuration in detail again. However we have to apple the new rule to attain stability so that the long-hand electron configuration for Chromium will be:

$1s^22s^22p^63s^23p^6\mathbf{4s^13d^5}$

> So for Cr, its short-hand version of its electron configuration would therefore be:
>
> $[Ar]\ 4s^13d^5$

d. Fe

Start off by identifying where Iron sits on the periodic table: row 4, group 8, meaning it has 26 electrons total. This is 5 elements to the right of the previous problem's Sc, so we will basically use the same method except, in the end, there will be 6 electrons remaining, so therefore the final orbital will be denoted as:

$3d^6$

If needed, look above to the exact steps for how to do it in detail again; the long-hand electron configuration for Iron will be:

$1s^22s^22p^63s^23p^64s^23d^6$

> So for Fe, its short-hand version of its electron configuration would therefore be:
>
> $[Ar]\ 4s^23d^6$

e. Ru

Start off by identifying where Ruthenium sits on the periodic table: row 5, group 8, that means it has a total of 44 electrons. But first, as stated earlier, Ru, along with Cr, Mo, Nb, Rh, Pd, Cu, Sg, Pt and Au, is a special case. You would think that since it has 44 electrons that its configuration would look like:

$1s^22s^22p^63s^23p^64s^23d^{10}4p^6\mathbf{5s^2\ 4d^6}$

> which is how we learned it earlier. However, this electron configuration is very unstable because of the fact that, even though there are 4 paired electrons, there are also 4 electrons unpaired. This results in a very unstable configuration, so to restore stability, we have to use a configuration that has the most paired electrons, which would be to take an electron from the s orbital and place it in the d orbital to create:
>
> $5s^14d^7$

If needed, look above to the exact steps for how to do the beginning of the configuration in detail again. However we have to apple the new rule to attain stability so that the long-hand electron configuration for Ru will be:

$1s^22s^22p^63s^23p^64s^23d^{10}4p^6\mathbf{5s^14d^7}$

> So for Cr, its short-hand version of its electron configuration would therefore be:
>
> $[Kr]\ 5s^14d^7$

2. Write the electron configurations for each of the following elements and its ions:

a. Ti

Titanium has an atomic number of 22, meaning it has 22 electrons. The noble gas prior to Titanium is Argon. Looking at row 4 of the periodic table, Titanium still has 4 electrons to be placed in orbitals since Argon has 18 electrons that are already placed. The remaining electrons will fill the $4s$ orbital and the remaining two electrons will go into the $3d$ orbital. [Ar]$4s^2 3d^2$

b. Ti^{+2}

This is an ion with a plus 2 charge, meaning 2 electrons have been removed. The electrons will be removed from the $4s$ orbital and the 2 remaining electrons will be placed in the $3d$ orbital. Like number 1, the prior noble gas is Argon. [Ar]$3d^2$

c. Ti^{+3}

This is an ion with a plus 3 charge, meaning 3 electrons have been removed. The first 2 electrons will be removed from the $4s$ orbital, and the third will be taken from the $3d$ orbital, and the 1 remaining electron will be placed in the 3d orbital. Like number 1, the prior noble gas is Argon. [Ar]$3d^1$

d. Ti^{+4}

This is an ion with a plus 4 charge, meaning 4 electrons have been removed. The first 2 electrons will be removed from the $4s$ orbital and the second 2 will be removed from the $3d$ orbital. This results in the ion having the same electron configuration as Argon. [Ar]

3. Write the electron configurations for each of the following elements and its 3+ ions:

a. La

b. Sm

c. Lu

Answer

La: [Xe]$6s^2 5d^1$, La^{3+}: [Xe]; Sm: [Xe]$6s^2 4f^6$, Sm^{3+}: [Xe]$4f^5$; Lu: [Xe]$6s^2 4f^{14} 5d^1$, Lu^{3+}: [Xe]$4f^{14}$

4. Indicate the coordination number for the central metal atom in each of the following coordination compounds:

a. $[Pt(H_2O)_2Br_2]$

Answer

a. The 2 aqua and the 2 bromo ligands form a total of 4 coordinate covalent bonds and as a result the coordination number is 4;

b. The ammine, pyridine, chloro and bromo each form one coordinate covalent bond that gives a total of 4 and hence CN=4;

c. Two ammine and two chloro ligands give a total of 4 coordinate covalent bonds and a CN = 4;

d. One ammine, a pyrimidine, a chloro and a bromo ligand give a total of 4 covalent bonds, resulting in CN = 4.;

e. Four aqua ligands and two chloro ligands form a total of 6 coordinate covalent bonds and a CN =6;

f. Ethylenediamine is a bidentate ligand that forms two coordinate covalent bonds and along with two cyano ligands it forma a total of 6 bonds. hence has a CN=6

b. $[Pt(NH_3)(py)(Cl)(Br)]$ (py = pyridine, C_5H_5N)

Answer

b. The ammine, pyridine, chloro and bromo each form one coordinate covalent bond that gives a total of 4 and hence CN=4;

c. $[Zn(NH_3)_2Cl_2]$

Answer

c. Two ammine and two chloro ligands give a total of 4 coordinate covalent bonds and a CN = 4;

d. $[Zn(NH_3)(py)(Cl)(Br)]$

Answer

d. One ammine, a pyrimidine, a chloro and a bromo ligand give a total of 4 covalent bonds, resulting in CN = 4.;

e. $[Ni(H_2O)_4Cl_2]$

Answer

e. Four aqua ligands and two chloro ligands form a total of 6 coordinate covalent bonds and a CN =6;

f. $[Fe(en)_2(CN)_2]^+$ (en = ethylenediamine, $C_2H_8N_2$)

Answer

f. Ethylenediamine is a bidentate ligand that forms two coordinate covalent bonds and along with two cyano ligands it forma a total of 6 bonds. hence has a CN=6

5. Give the coordination numbers and write the formulas for each of the following, including all isomers where appropriate:

a. tetrahydroxozincate(II) ion (tetrahedral)
b. hexacyanopalladate(IV) ion
c. dichloroaurate ion (note that *aurum* is Latin for "gold")
d. diaminedichloroplatinum(II)
e. potassium diaminetetrachlorochromate(III)
f. hexaaminecobalt(III) hexacyanochromate(III)
g. dibromobis(ethylenediamine) cobalt(III) nitrate

Answer

To determine coordination numbers we must count the total number of ligands bonded to the central metal and distinguish monodentate and polydentate ligands. To determine the formulas, we use the nomenclature rules and work backwards.

a. "tetrahydroxo" = 4 hydroxide ligands, since hydroxide is a monodentate ligand, we have a total of 4 bonds to the central metal
Coordination Number: 4
Since the charge on Zinc is 2+ which is given in the nomenclature by the roman numerals, we can calculate the total charge on the complex is 2-
Formula: $[Zn(OH)_4]^{2-}$

b. "hexacyano" = 6 cyanide ligands, since cyanide is a monodentate ligand, we have a total of 6 bonds to the central metal
Coordination Number: 6
We review the basics of nomenclature and see that "hexa" = 6 and "cyano" = CN^-. Since the charge on Pd is 4+ which is given in the nomenclature by the roman numerals, we can calculate the total charge on the complex is 2-
Formula: $[Pd(CN)_6]^{2-}$

c. "dicholor" = 2 chloride ligands, since chloride is a monodentate ligand, we have a total of 2 bonds to the central metal
Coordination Number: 2
We review the basics of nomenclature and see that "di" = 2 and "chloro" = Cl^-. Since the charge on Au is always 1+, we can calculate the total charge on the complex is 1-
Formula: $[AuCl_2]^-$

d. "diamine" = 2 ammonia ligands and "dichloro" = 2 chloride ligands, since both ammonia and chloride ligands are monodentant, we have a total of 4 bonds to the central metal
Coordination Number: 4

e. 6, $[Co(NH_3)_6][Cr(CN)_6]$;

f. 6, $[Co(en)_2Br_2]NO_3$

6. Give the coordination number for each metal ion in the following compounds:

a. $[Co(CO_3)_3]^{3-}$ (note that $CO_3{}^{2-}$ is bidentate in this complex)
b. $[Cu(NH_3)_4]^{2+}$
c. $[Co(NH_3)_4Br_2]_2(SO_4)_3$
d. $[Pt(NH_3)_4][PtCl_4]$
e. $[Cr(en)_3](NO_3)_3$
f. $[Pd(NH_3)_2Br_2]$ (square planar)
g. $K_3[Cu(Cl)_5]$
h. $[Zn(NH_3)_2Cl_2]$

Answer

You can determine a compound's coordination number based on how many ligands are bound to the central atom.

a. In this compound, Cobalt is the central atom, and it has 3 CO_3^{2-} molecules attached to it. However, CO_3^{2-} is a bidentate ligand, which means it binds to the central atom in two places rather than one. This means that the coordination number of $[Co(CO_3)_3]^{3-}$ is 6. A coordination number of 6 means that the structure is most likely octahedral.

b. In this compound, Copper is the central atom. 4 ammonia molecules are attached to it. This means the coordination number is 4, and the structure is likely tetrahedral.

c. For this compound, we can ignore the $(SO_4)_3$ because it is not bound to the central atom. The central atom is cobalt, and it has 4 ammonia molecules and 2 bromine molecules bound to it. The coordination number is 6.

d. There are two compounds here, indicated by the brackets. The central atom for both is platinum. One of them has 4 ammonia molecules attached, and the other has 4 chlorine atoms attached. Both complexes have a coordination number of 4.

e. We can ignore $(NO_3)_3$ for this compound. The central atom is Chromium. There are 3 ethylenediamine molecules attached to the chromium. Ethylenediamine is a bidentate ligand, so the coordination number is 6.

f. Palladium is the central atom. 2 ammonia molecules and 2 bromine atoms are bound to the palladium atom. The coordination number is 4.

g. We can ignore the K_3 structure. Copper is the central atom, and there are 5 chlorine molecules attached to it. The coordination number is 5, so the structure is either trigonal bipyramidal or square pyramidal.

h. In this compound, zinc is the central atom. There are 2 ammonia molecules and 2 chlorine atoms attached. This means that the coordination number is 4.

7. Sketch the structures of the following complexes. Indicate any *cis*, *trans*, and optical isomers.

a. $[Pt(H_2O)_2Br_2]$ (square planar)
b. $[Pt(NH_3)(py)(Cl)(Br)]$ (square planar, py = pyridine, C_5H_5N)
c. $[Zn(NH_3)_3Cl]^+$ (tetrahedral)
d. $[Pt(NH_3)_3Cl]^+$ (square planar)
e. $[Ni(H_2O)_4Cl_2]$
f. $[Co(C_2O_4)_2Cl_2]^{3-}$ (note that $C_2O_4^{2-}$ is the bidentate oxalate ion, $-O_2CCO_2^-$)

Hint

Cis and trans are a type of geometric isomer, meaning there is a difference in the orientation in which the ligands are attached to the central metal. In cis, two of the same ligands are adjacent to one another and in trans, two of the same ligands are directly across from one another.

Optical isomers → have the ability to rotate light, optical isomers are also chiral. Only chiral complexes have optical isomers

Chiral → asymmetric, structure of its mirror image is not superimposable

Enantiomers: chiral optical isomers (compound can have multiple enantiomers)

Tetrahedral complex with 4 distinct ligands → always chiral

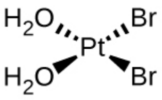
For tetrahedral, if 2 ligands are the same, then it cannot be chiral, has a plane of symmetry

Solutions:

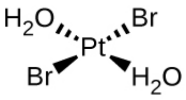
Answer

a. $[Pt(H_2O)_2Br_2]$ (square planar)

This complex has 2 kinds of ligands. The matching ligands can either be adjacent to each other and be cis, or they can be across from each other and be trans.



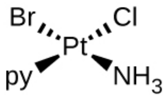
cis

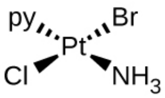


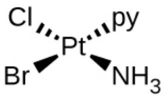
trans

b. $[Pt(NH_3)(py)(Cl)(Br)]$ (square planar, py = pyridine, C_5H_5N)

This complex has 4 different ligands. There is no plane of symmetry in any of the enantiomers, making the structures chiral and therefore has optical isomers.

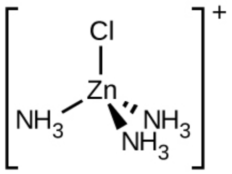






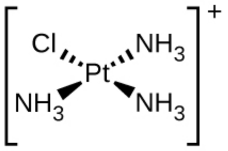
c. $[Zn(NH_3)_3Cl]^+$ (tetrahedral)

There is a plane of symmetry from NH_3 through Zn to the other NH_3, therefore it is not chiral.



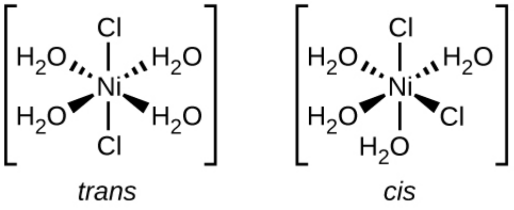
d. $[Pt(NH_3)_3Cl]^+$ (square planar)

There is a plane of symmetry from NH_3 through Pt to the other NH_3, therefore it is not chiral.



e. $[Ni(H_2O)_2Cl_2]$

The Cl ligands can either be right next to each other, or directly across from one another allowing for both cis and trans geometries.

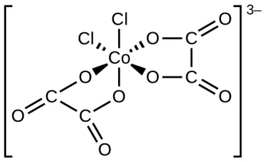


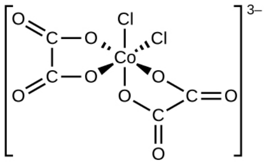
trans

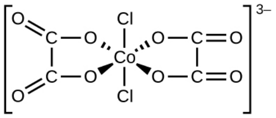
cis

f. $[Co(C_2O_4)_2Cl_2]^-3$ (note that $C_2O_4^-2$ is the bidentate oxalate ion, $^-O_2CCO_2^-$

There is a plane of symmetry from Cl through Co to the other Cl in a "trans" chlorine configuration, therefore it is not chiral in a chlorine "trans" configuration. However, there is no symmetry in the chlorine "cis" configuration, indicating multiple "cis" isomers.







8. Draw diagrams for any *cis*, *trans*, and optical isomers that could exist for the following (en is ethylenediamine):

  a. $[Co(en)_2(NO_2)Cl]^+$
  b. $[Co(en)_2Cl_2]^+$
  c. $[Pt(NH_3)_2Cl_4]$
  d. $[Cr(en)_3]^{3+}$
  e. $[Pt(NH_3)_2Cl_2]$

Hint

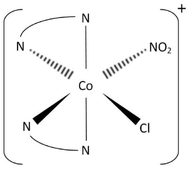
We are instructed to draw all geometric isomers and optical isomers for the specified compound. Optical isomers exist when an isomer configuration is not superimposable on its mirror image. This means there are two distinct molecular shapes. Often a left and right hand are cited as an example; if you were to take your right hand and place it upon your left, you cannot make the major parts of your hand align on top of one another. The basic idea when deciding whether something is optically active is to look for a plane of symmetry--if you are able to bisect a compound in a manner that establishes symmetry, then the compound does not have an optical isomer.

Cis isomers exist when there are 2 ligands of the same species placed at 90 degree angles from each other. Trans isomers exist when there are 2 ligands of the same species placed at 180 degree angles from each other.

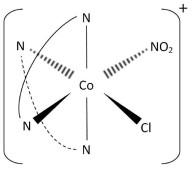
Problem 1

Answer

a. This compound is an octahedral molecule, so the six ligands (atoms in the complex that are not the central transition metal) are placed around the central atom at 90 degree angles. Two optical isomers exist for $[Co(en)_2(NO_2)Cl]^+$. The second isomer is drawn by taking the mirror image of the first.

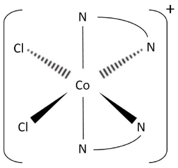


Optical isomer 1

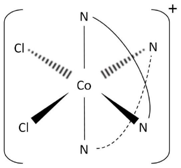


Optical isomer 2

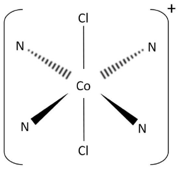
b. This compound is also an octahedral molecule. Two cis (optical) isomers and one trans isomer exist for $[Co(en)_2Cl_2]^+$. The trans isomer can be drawn by placing the chlorine ligands in positions where they form a 180 degree angle with the central atom. The first cis isomer can be drawn by placing the chlorine ligands in positions where they form a 90 degree angle with the central atom. The second cis isomer can be found by mirroring the first cis isomer, like we did in a.



Cis isomer (Optical 1)

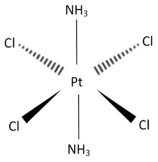


Cis isomer (Optical 2)

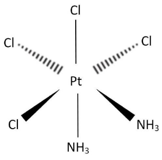


Trans isomer

c. This compound is also an octahedral molecule. One trans isomer and one cis isomer of $[Pt(NH_3)_2Cl_4]$ exist. The trans isomer can be drawn by placing the ammonia ligands in positions where they form a 180 degree angle with the central atom. The cis isomer can be drawn by placing the ammonia ligands in positions where they form a 90 degree angle with the central atom.

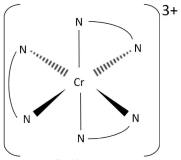


Trans isomer

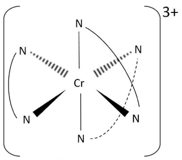


Cis isomer

d. This compound is also an octahedral molecule. Two optical isomers for $[Cr(en)_3]^{3+}$ exist. The second optical isomer can be drawn by taking the mirror image of the first optical isomer.

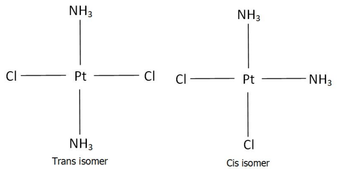


Optical isomer 1



Optical isomer 2

e. This compound is a square planar complex, so the ligands are placed around the central atom in a plane, at 90 angles. A trans isomer and a cis isomer exist for the complex $[Pt(NH_3)_2Cl_2]$. The trans isomer can be drawn by placing the ammonia ligands in positions where they form a 180 degree angle in the plane with the central atom. The cis isomer can be drawn by placing the ammonia ligands in positions where they form a 90 degree angle in the plane with the central atom.



9. Name each of the compounds or ions given in Exercise 6, including the oxidation state of the metal.

Hint

Rules to follow for coordination complexes

1. Cations are always named before the anions.
2. Ligands are named before the metal atom or ion.
3. Ligand names are modified with an -o added to the root name of an anion. For neutral ligands the name of the molecule is used, with the exception of OH2, NH3, CO and NO.
4. The prefixes mono-, di-, tri-, tetra-, penta-, and hexa- are used to denote the number of simple ligands.
5. The prefixes bis-, tris-, tetrakis-, etc., are used for more complicated ligands or ones that already contain di-, tri-, etc.
6. The oxidation state of the central metal ion is designated by a Roman numeral in parentheses.
7. When more than one type of ligand is present, they are named alphabetically. Prefixes do not affect the order.
8. If the complex ion has a negative charge, the suffix –ate is added to the name of the metal.
9. In the case of complex-ion isomerism the names cis, trans, fac, or mer may precede the formula of the complex-ion name to indicate the spatial arrangement of the ligands. Cis means the ligands occupy adjacent coordination positions, and trans means opposite positions just as they do for organic compounds. The complexity of octahedral complexes allows for two additional geometric isomers that are peculiar to coordination complexes. Fac means facial, or that the three like ligands occupy the vertices of one face of the octahedron. Mer means meridional, or that the three like ligands occupy the vertices of a triangle one side of which includes the central metal atom or ion.

Answer

a. tricarbonatocobaltate(III) ion;

b. tetraaminecopper(II) ion;

c. tetraaminedibromocobalt(III) sulfate;

d. tetraamineplatinum(II) tetrachloroplatinate(II);

e. *tris*-(ethylenediamine)chromium(III) nitrate;

f. diaminedibromopalladium(II);

g. potassium pentachlorocuprate(II);

h. diaminedichlorozinc(II)

10. Name each of the compounds or ions given in Exercise 8.

Answer

a. Chlorobis(ethylenediamine)nitrocobalt(III)

b. Dichlorobis(Ethylenediamine)cobalt(III)

c. Diamminetetrachloroplatinum(IV)

d. Tris(ethylenediamine)cromium(III)

e. Diamminedichloroplatinum(II)

11. Specify whether the following complexes have isomers.

a. tetrahedral $[Ni(CO)_2(Cl)_2]$
b. trigonal bipyramidal $[Mn(CO)_4NO]$
c. $[Pt(en)_2Cl_2]Cl_2$

Answer

a. none;

b. none;

c. The two Cl ligands can be *cis* or *trans*. When they are *cis*, there will also be an optical isomer.

12. Predict whether the carbonate ligand CO_3^{2-} will coordinate to a metal center as a monodentate, bidentate, or tridentate ligand.

Answer

CO_3^{-2} will coordinate to a metal center as a monodentate ligand.

13. Draw the geometric, linkage, and ionization isomers for $[CoCl_5CN][CN]$.

Hint

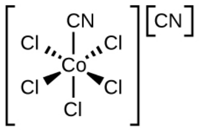
Isomers are compounds with same formula but different atom arrangement. There are two subcategories: **structural isomers**, which are isomers that contain the same number of atoms of each kind but differ in which atoms are bonded to one another, and **stereoisomers**, isomers that have the same molecular formula and ligands, but differ in the arrangement of those ligands in 3D space.

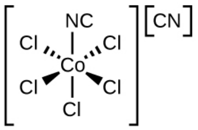
There are three subcategories under structural isomers: **ionization isomers**, which are isomers that are identical except for a ligand has exchanging places with an anion or neutral molecule that was originally outside the coordination complex; **coordination isomers**, isomers that have an interchange of some ligands from the cationic part to the anionic part; and **linkage isomers**, in two or more coordination compounds in which the donor atom of at least one of the ligands is different.

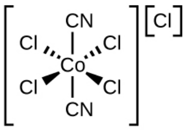
There are also two main kinds of stereoisomers: **geometric isomers**, metal complexes that differ only in which ligands are adjacent to one another (cis) or directly across from one another (trans) in the coordination sphere of the metal, and **optical isomers**, which occurs when the mirror image of an object is non-superimposable on the original object.

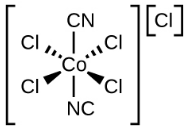
Some of the isomers look almost identical, but that is because the CN ligand can be attached by both (but not at the same time) the C or N.

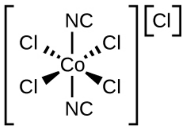
Answer

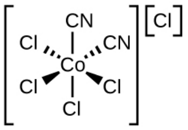


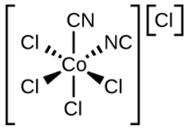


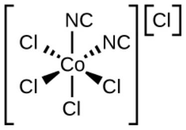












2.7.1: Spectroscopic and Magnetic Properties of Coordination Compounds

14. Determine the number of unpaired electrons expected for $[Fe(NO_2)_6]^{3-}$and for $[FeF_6]^{3-}$ in terms of crystal field theory.

Hint

The crystal field theory is is a model that describes the breaking of degeneracies of electron orbital states, usually d or f orbitals, due to a static electric field produced by a surrounding charge distribution.

The degenerate d-orbitals split into two levels, e_g and t_{2g}, in the presence of ligands.

The energy difference between the two levels is called the crystal-field splitting energy, $\Delta_\circ$.

After 1 electron each has been filled in the three t_{2g} orbitals, the filling of the fourth electron takes place either in the e_g orbital or in the t_{2g}, where the electrons pair up. depending on whether the complex is high spin or low spin.

If the $\Delta_\circ$ value of a ligand is less than the pairing energy (P), then the electrons enter the e_g orbital, but if the $\Delta_\circ$ value of a ligand is more than the pairing energy (P), then the electrons enter the t_{2g} orbital.

when the Δ_o is less than the pairing energy, the electrons prefer then e_g orbitals because there is not enough energy to pair the electrons together. It will be **high** spin when the Δ_o is more then the pairing energy, the electrons prefer the t_{2g} because there is enough energy to pair the electrons. It will be **low** spin.

Step 1: Determine the oxidation state of the Fe

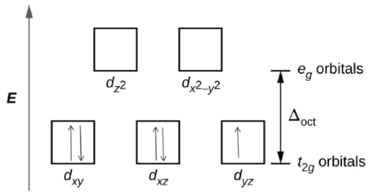
For $[Fe(NO_2)_6]^{3-}$ and $[FeF_6]^{3-}$, both NO_2 and F_6 have a charge of -1. Since there is 6 of them then that means the charge is -6 and in order for there to be an overall charge of -3, Fe has to have a +3 charge.

Step 2: Determine type of ligand

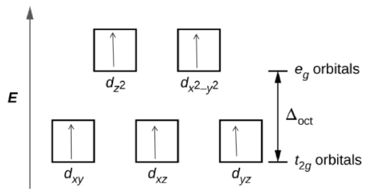
Based on the spectrochemical series we can see that NO_2^- is a stronger field ligand than F^-, and therefore is a low spin complex because it has a high $\Delta_\circ$ unlike F^- which is a high spin.

Step 3: Draw the crystal field

$[Fe(NO_2)_6]^{3-}$



$[FeF_6]^{3-}$



There is 1 unpaired electron for $[Fe(NO_2)_6]^{3-}$, and 5 for $[FeF_6]^{3-}$ based on the crystal field theory.

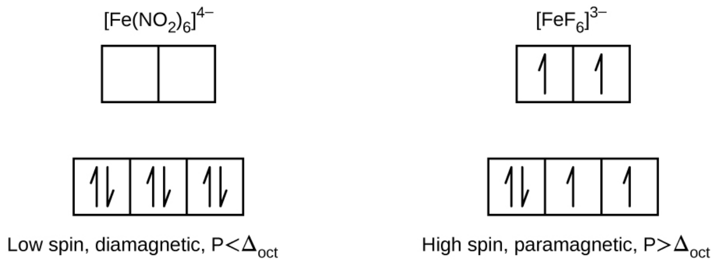
Answer

$[Fe(NO_2)_6]^{3-}$:1 electron

$[FeF_6]^{3-}$:5 electrons

15. Draw the crystal field diagrams for $[Fe(NO_2)_6]^{4-}$ and $[FeF_6]^{2-}$. State whether each complex is high spin or low spin, paramagnetic or diamagnetic, and compare Δ_{oct} to P for each complex.

Answer



16. Give the oxidation state of the metal, number of *d* electrons, and the number of unpaired electrons predicted for $[Co(NH_3)_6]Cl_3$.

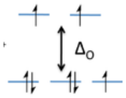
Answer

a. The ox state is 3+, there are 6 d electrons, there are no unpaired electrons

17. The solid anhydrous solid $CoCl_2$ is blue in color. Because it readily absorbs water from the air, it is used as a humidity indicator to monitor if equipment (such as a cell phone) has been exposed to excessive levels of moisture. Predict what product is formed by this reaction, and how many unpaired electrons this complex will have.

Answer

$[Co(H_2O)_6]Cl_2$ with three unpaired electrons.



18. Is it possible for a complex of a metal in the transition series to have six unpaired electrons? Explain.

Answer

It is not possible for a metal in the transition series to have six unpaired electrons. This is because transition metals have a general electron configuration of $(n\text{-}1)d^{1\text{-}10}$ $ns^{1\text{-}2}$ where n is the quantum number. The last electron will go into the d orbital which has 5 orbitals that can each contain 2 electrons, yielding 10 electrons total. According to Hund's Rule, electrons prefer to fill each orbital singly before they pair up. This is more energetically favorable. Since there are only 5 orbitals and due to Hund's Rule, the maximum number of unpaired electrons a transition metal can have is 5. Therefore, there cannot be a complex of a transition metal that has 6 unpaired electrons.

For example, lets look at iron's electron configuration. Iron has an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. Now the most important orbital to look at is the d orbital which has 6 electrons in it, but there are only 4 unpaired electrons as you can see by this diagram:

3d: [↿ ⇂] [↿] [↿][↿][↿]

Each [ ] represents an orbital within the d orbital. This diagram follows Hund's rule and shows why no transition metal can have 6 unpaired electrons.

19. How many unpaired electrons are present in each of the following?

a. $[CoF_6]^{3-}$ (high spin)
b. $[Mn(CN)_6]^{3-}$ (low spin)
c. $[Mn(CN)_6]^{4-}$ (low spin)
d. $[MnCl_6]^{4-}$ (high spin)
e. $[RhCl_6]^{3-}$ (low spin)

Answer

a. 4; b. 2; c. 1; d. 5; e. 0

20. Explain how the diphosphate ion, $[O_3P{-}O{-}PO_3]^{4-}$, can function as a water softener that prevents the precipitation of Fe^{2+} as an insoluble iron salt.

Answer

The diphosphate ion, $[O_3P{-}O{-}PO_3]^{4-}$ can function as a water softener keeping the iron in a water soluble form because of its more negative electrochemical potential than water's. This is similar to the way plating prevents metals from reacting with oxygen to corrode.

Mineral deposits are formed by ionic reactions. The Fe^{2+} will form an insoluble iron salt of iron(III) oxide-hydroxide when a salt of ferric iron hydrolyzes water. However, with the addition of $[O_3P{-}O{-}PO_3]^{4-}$, the Fe^{2+} cations are more attracted to the PO_3 group, forming a $Fe(PO_3)$ complex.

The excess minerals in this type of water is considered hard thus its name hard water.

21. For complexes of the same metal ion with no change in oxidation number, the stability increases as the number of electrons in the t_{2g} orbitals increases. Which complex in each of the following pairs of complexes is more stable?

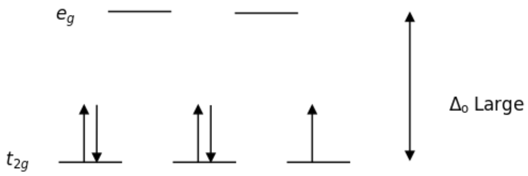
a. $[Fe(H_2O)_6]^{2+}$ or $[Fe(CN)_6]^{4-}$
b. $[Co(NH_3)_6]^{3+}$ or $[CoF_6]^{3-}$
c. $[Mn(CN)_6]^{4-}$ or $[MnCl_6]^{4-}$

Hint

The Spectrochemical Series is as follows

$$I^- < Br^- < SCN^- \approx Cl^- < F^- < OH^- < ONO^- < ox < H_2O < SCN^- < EDTA < NH_3 < en < NO_2^- < CN \tag{2.7.1}$$

The strong field ligands (on the right) are low spin which fills in more electrons in the t_{2g} orbitals. The weak field ligands (on the left) are high spin so it can fill electrons in the t_{2g} orbitals and e_g orbitals. In conclusion, more electrons are filled up from the strong field ligands because the electrons don't move up to the e_g orbitals.



Answer

a. $[Fe(CN)_6]^{4-}$; b. $[Co(NH_3)_6]^{3+}$; c. $[Mn(CN)_6]^{4-}$

2.7.1.1: Q19.3.9

Trimethylphosphine, $P(CH_3)_3$, can act as a ligand by donating the lone pair of electrons on the phosphorus atom. If trimethylphosphine is added to a solution of nickel(II) chloride in acetone, a blue compound that has a molecular mass of approximately 270 g and contains 21.5% Ni, 26.0% Cl, and 52.5% $P(CH_3)_3$ can be isolated. This blue compound does not have any isomeric forms. What are the geometry and molecular formula of the blue compound?

2.7.1.2: S19.3.9

1)Find the empirical formula. There is a total of 270 grams. To find out how many grams of each element/compound there are, multiply the percentage by the mass (270).

$$(270g)(0.215) = 58.05gNi \tag{2.7.2}$$

$$(270g)(0.26) = 70.2gCl \tag{2.7.3}$$

$$(270g)(0.525) = 141.75gP(CH_3)_3 \tag{2.7.4}$$

Now that we have the grams of each element/compound, we can convert them to moles by using their molar mass.

$$(58.055gNi)(\frac{1mol.}{58.69gNi}) = 0.989mol.\,Ni \tag{2.7.5}$$

$$(70.2gCl)(\frac{1mol.}{35.45gCl}) = 1.98mol.\,Cl \tag{2.7.6}$$

$$(141.75gP(CH_3)_3)(\frac{1mol.}{76.07gP(CH_3)_3}) = 1.86mol.\,P(CH_3)_3 \tag{2.7.7}$$

Now that we have the moles of all elements/compounds, we can find the ratio of all them to each other. To do this, we take the element/compound with the least amount of moles and divide all element/compound moles by this amount. In this case, Ni has the least number of moles.

$$\frac{0.989mol.\,Ni}{0.989mol.\,Ni} = 1 \tag{2.7.8}$$

$$\frac{1.98mol.\,Cl}{0.989mol.\,Ni} = approx.2 \tag{2.7.9}$$

$$\frac{1.86mol.\,P(CH_3)_3}{0.989mol.\,Ni} = approx.2 \tag{2.7.10}$$

We now know the ratio of all element/compounds in the blue compound.

The empirical formula is: $NiCl(P(CH_3)_3)_2$

This formula shows us there are 4 ligands. There are 2 chlorine ligands and 2 trimethylphosphine ligands. This means that the blue compound has either a tetrahedral or square planar shape, where tetrahedral shapes are capable of different isomeric forms when all ligands are different (because if not, there is only 1 way for them to be arranged), and square planar shapes are capable of cis/trans forms. In the problem, it states this compound does not have any isomeric forms, therefore this has a tetrahedral shape.

2.7.1.3: A19.3.9

a) $NiCl(P(CH_3)_3)_2$

b) Tetrahedral

2.7.1.4: Q19.3.10

Would you expect the complex $[Co(en)_3]Cl_3$ to have any unpaired electrons? Any isomers?

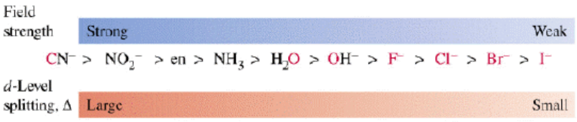
2.7.1.5: S19.3.10

Assign oxidation states to each element. Cl- has a -1 oxidation state. En is neutral, so 0. The entire complex is also neutral, so in order to balance the charges out, Co must be +3 because there are 3 chlorides, which gives a -3 charge.

STEP 2:

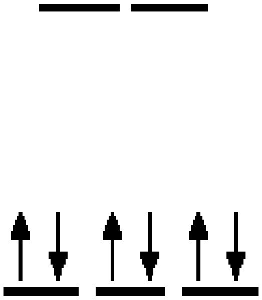
Write the electron configuration for Co^{3+}. $[Ar]3d^6$. There are 6 electrons.

STEP 3:



Check where en lies on the spectrochemical series. Does it have a strong field strength? It does, so these electrons will exist at the d-level with high splitting energy because the magnitude of the pairing energy is less than the crystal field splitting energy in the octahedral field.

You will the notice that there aren't any unpaired electrons when you draw the Crystal Field Theory (CFT) diagram.



This complex does not have any geometric isomers because cis-trans structures cannot be formed. The mirror image is nonsuperimpoasable, which means the enantiomers are chiral molecules; if the mirror image is placed on top on the original molecule, then they will never be perfectly aligned to give the same molecule.

2.7.1.6: A19.3.10

The complex does not have any unpaired electrons. The complex does not have any geometric isomers, but the mirror image is nonsuperimposable, so it has an optical isomer.

2.7.1.7: Q19.3.11

Would you expect the $Mg_3[Cr(CN)_6]_2$ to be diamagnetic or paramagnetic? Explain your reasoning.

2.7.1.8: S19.3.11

The first step to determine the magnetism of the complex is to calculate the oxidation state of the transition metal. In this case, the transition metal is Cr.

Before doing so, we need to find charge of the of the complex ion $[Cr(CN)_6]_2$ given that the oxidation state of Mg_3 is 2+. Using the subscripts of the Mg^{2+} ion and the $[Cr(CN)_6]_2$ complex, we find that the oxidation state of $[Cr(CN)_6]_2$, x, to be:

$3(+2)+2(x)=0$

$x=3$

Now that we found the charge of the coordination complex, we are able to find the charge of the transition metal Cr given that the charge of CN is -1. Again, using the subscripts we find the oxidation state of Cr, y, to be:

$y+6(-1)=-3$

$y=3$

Therefore, the oxidation state of the transition metal Cr is Cr^{3+}

> Next, using the transition metal Cr^{3+} and the periodic table as reference, we can determine the electron configuration of Cr^{3+} to be $[Ar]d^3$. This means that Cr^{3+} has 3 unpaired electrons in the 3d sublevel. Therefore, we find that since at least one electron is unpaired(in this case all 3 electrons are unpaired), $Mg_3[Cr(CN)_6]_2$ is paramagnetic.

A19.3.11

a) Paramagnetic

2.7.1.9: Q19.3.12

Would you expect salts of the gold ion, Au^+, to be colored? Explain.

2.7.1.10: S19.3.12

No. **Colored ions have unpaired electrons in their outmost orbital**. A partially filled d orbital, for example, can yield various colors. After completing the noble gas configuration, we see that Au^+ has a configuration of [Xe] $4f^{14}$**$5d^{10}$**. Since Au^+ has a **completely filled d sublevel**, we are certain that any salts of the gold ion, Au^+ will be **colorless.**

*An example of a colored ion would be copper(II). Cu^{2+} has an electron configuration of $[Ar]3d^9$. It has one unpaired electron. Copper(II) appears blue.

2.7.1.11: A19.3.12

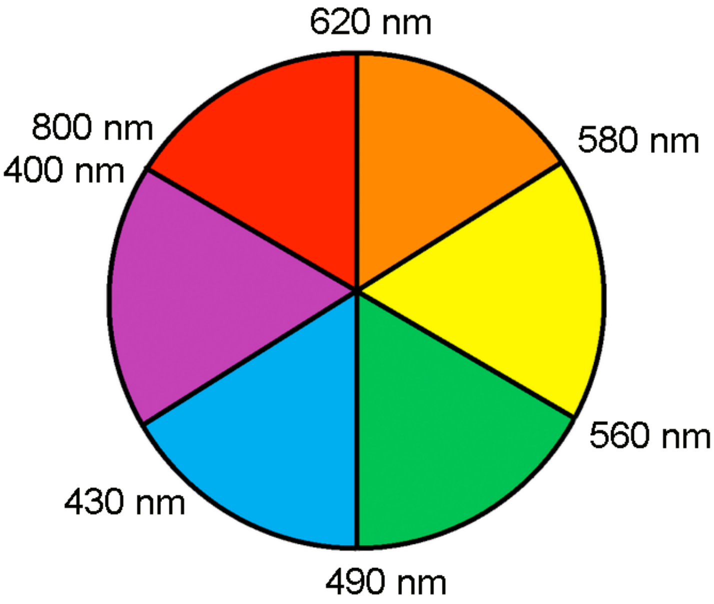
No. Au^+ has a complete 5*d* sublevel.

2.7.1.12: Q19.3.13

$[CuCl_4]^{2-}$ is green. $[Cu(H_2O)_6]^{2+}$is blue. Which absorbs higher-energy photons? Which is predicted to have a larger crystal field splitting?

2.7.1.13: S19.3.13

Although a color might appear a certain way, it actual absorbs a different color, opposite of it on the color wheel.

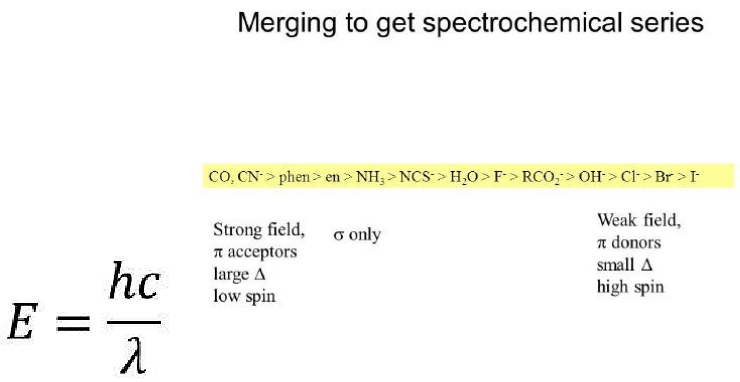


In this case;

$[CuCl_4]^{2-}$ appears green but is opposite of red on the color wheel which is absorbed and is characterized by wavelengths 620-800 nanometers.

$[Cu(H_2O)_6]^{2+}$ appears blue but is opposite of orange on the color wheel which is absorbed and is characterized by wavelengths 580-620 nanometers.

When determining which absorbs the higher energy photons, one must look at the complex itself. A higher energy indicates a high energy photon absorbed and a lower energy indicates a lower energy photon absorbed. How can we determine this? By looking at the complex and more specifically the ligand attached and its location in the spectrochemical series.



The ligands attached are Water and Chlorine and since Water is a stronger ligand than Chlorine according to the series, it also has larger energy, indicating a higher energy. This means that the complex $[Cu(H_2O)_6]^{2+}$ absorbs a higher energy photon because of its a stronger ligand than chlorine.

Part 2 of this question also asks which complex is predicted to have a larger crystal field splitting. To determine this you also use the spectrochemical series and see which ligand is stronger. Since H_2O is stronger than Cl^- on the spectrochemical series, we can say $[Cu(H_2O)_6]^{2+}$ has a higher crystal field splitting.

2.7.1.14: A19.3.13

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

b) $[Cu(H_2O)_6]^{2+}$ has a higher crystal field splitting

CHAPTER OVERVIEW

3: Chemical Kinetics

3.1: Chemical Reaction Rates

Learning Objectives

- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data

A *rate* is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The rate of reaction is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

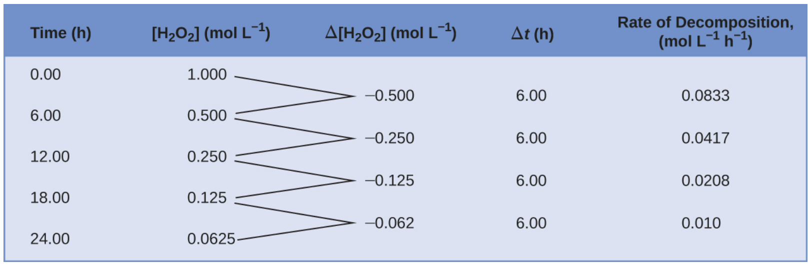
For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. If we measure the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution, we find that it changes slowly over time as the H_2O_2 decomposes, according to the equation:

$$2\,\mathrm{H_2O_2}(aq) \longrightarrow 2\,\mathrm{H_2O}(l) + \mathrm{O_2}(g)$$

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\begin{aligned} \text{rate of decomposition of } \mathrm{H_2O_2} &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= -\frac{[\mathrm{H_2O_2}]_{t_2} - [\mathrm{H_2O_2}]_{t_1}}{t_2 - t_1} \\ &= -\frac{\Delta[\mathrm{H_2O_2}]}{\Delta t} \end{aligned}$$

This mathematical representation of the change in species concentration over time is the rate expression for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates "change in." Thus, $[\mathrm{H_2O_2}]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time t_1; likewise, $[\mathrm{H_2O_2}]_{t_2}$ represents the molar concentration of hydrogen peroxide at a later time t_2; and $\Delta[H_2O_2]$ represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[H_2O_2]$ is a negative quantity; we place a negative sign in front of the expression because reaction rates are, by convention, positive quantities. Figure 3.1.1 provides an example of data collected during the decomposition of H_2O_2.



Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol L^{-1} h^{-1})
0.00	1.000			
		−0.500	6.00	0.0833
6.00	0.500			
		−0.250	6.00	0.0417
12.00	0.250			
		−0.125	6.00	0.0208
18.00	0.125			
		−0.062	6.00	0.010
24.00	0.0625			

Figure 3.1.1: The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases.

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$\frac{-\Delta[\mathrm{H_2O_2}]}{\Delta t} = \frac{-(0.500\ \mathrm{mol/L} - 1.000\ \mathrm{mol/L})}{(6.00\ \mathrm{h} - 0.00\ \mathrm{h})} = 0.0833\ \mathrm{mol\ L^{-1}\ h^{-1}} \tag{3.1.1}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

$$\frac{-\Delta[\mathrm{H_2O_2}]}{\Delta t} = \frac{-(0.0625\ \mathrm{mol/L} - 0.125\ \mathrm{mol/L})}{(24.00\ \mathrm{h} - 18.00\ \mathrm{h})} = 0.0104\ \mathrm{mol\ L^{-1}\ h^{-1}} \tag{3.1.2}$$

This behavior indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an average rate for the reaction over this time interval. At any specific time, the rate at which a reaction is proceeding is known as its instantaneous rate. The instantaneous rate of a reaction at "time zero," when the reaction commences, is its initial rate. Consider the analogy of a car slowing down as it approaches a stop sign. The vehicle's initial rate—analogous to the beginning of a chemical reaction—would be the speedometer reading at the moment the driver begins pressing the brakes (t_0). A few moments later, the instantaneous rate at a specific moment—call it t_1—would be somewhat slower, as indicated by the speedometer reading at that point in time. As time passes, the instantaneous rate will continue to fall until it reaches zero, when the car (or reaction) stops. Unlike instantaneous speed, the car's average speed is not indicated by the speedometer; but it can be calculated as the ratio of the distance traveled to the time required to bring the vehicle to a complete stop (Δt). Like the decelerating car, the average rate of a chemical reaction will fall somewhere between its initial and final rates.

The instantaneous rate of a reaction may be determined one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible. If we plot the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of H_2O_2 at any time t is given by the slope of a straight line that is tangent to the curve at that time (Figure 3.1.2). We can use calculus to evaluate the slopes of such tangent lines, but the procedure for doing so is beyond the scope of this chapter.

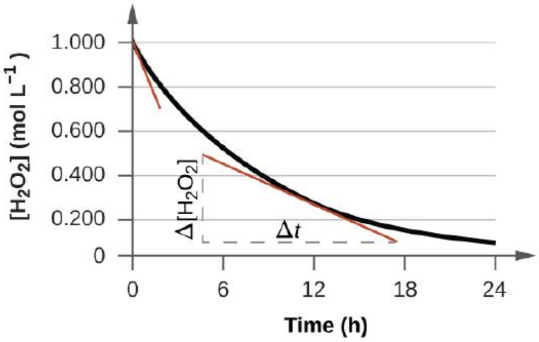


Figure 3.1.2: This graph shows a plot of concentration versus time for a 1.000 M solution of H_2O_2. The rate at any instant is equal to the opposite of the slope of a line tangential to this curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 10 h ("instantaneous rate" at that particular time).

Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (Figure 3.1.3). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in color upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:

$$\mathrm{C_6H_{12}O_6 + O_2 \xrightarrow[\text{catalyst}]{} C_6H_{10}O_6 + H_2O_2} \tag{3.1.3}$$

$$\mathrm{2\,H_2O_2 + 2\,I^- \xrightarrow[\text{catalyst}]{} I_2 + 2\,H_2O + O_2} \tag{3.1.4}$$

Equation 3.1.3 depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine (Equation 3.1.4), which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change.

The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis*, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the color-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the color change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.

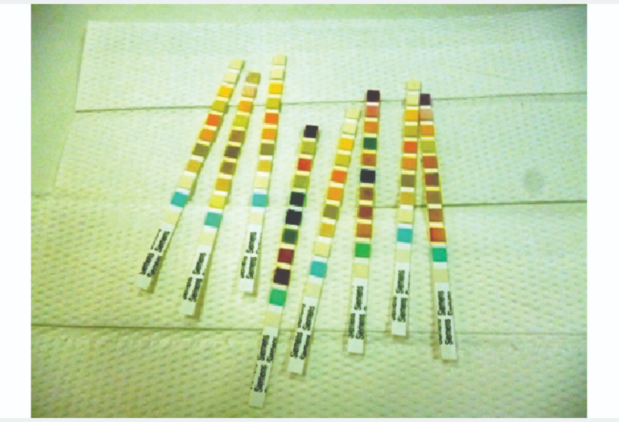


Figure 3.1.3: Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman).

3.1.1: Relative Rates of Reaction

The rate of a reaction may be expressed in terms of the change in the amount of any reactant or product, and may be simply derived from the stoichiometry of the reaction. Consider the reaction represented by the following equation:

$$2\,NH_3(g) \longrightarrow N_2(g) + 3\,H_2(g) \tag{3.1.5}$$

The stoichiometric factors derived from this equation may be used to relate reaction rates in the same manner that they are used to related reactant and product amounts. The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta \text{mol NH}_3}{\Delta t} \times \frac{1 \text{ mol N}_2}{2 \text{ mol NH}_3} = \frac{\Delta \text{mol N}_2}{\Delta t} \tag{3.1.6}$$

We can express this more simply without showing the stoichiometric factor's units:

$$-\frac{1}{2}\frac{\Delta \text{mol NH}_3}{\Delta t} = \frac{\Delta \text{mol N}_2}{\Delta t} \tag{3.1.7}$$

Note that a negative sign has been added to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). If the reactants and products are present in the same solution, the molar amounts may be replaced by concentrations:

$$-\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = \frac{\Delta[N_2]}{\Delta t} \tag{3.1.8}$$

Similarly, the rate of formation of H_2 is three times the rate of formation of N_2 because three moles of H_2 form during the time required for the formation of one mole of N_2:

$$\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[N_2]}{\Delta t} \tag{3.1.9}$$

Figure 3.1.4 illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. We can see from the slopes of the tangents drawn at t = 500 seconds that the instantaneous rates of change in the concentrations of the reactants and products are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

$$\frac{2.91 \times 10^{-6}\ M/\mathrm{s}}{9.71 \times 10^{-6}\ M/\mathrm{s}} \approx 3 \tag{3.1.10}$$

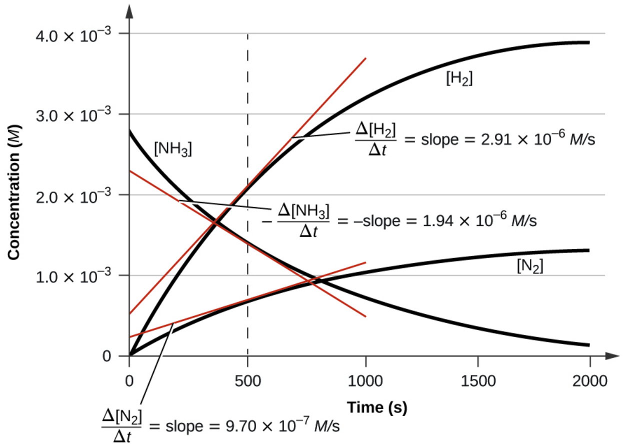


Figure 3.1.4: This graph shows the changes in concentrations of the reactants and products during the reaction $2\,\mathrm{NH_3} \longrightarrow \mathrm{N_2} + 3\,\mathrm{H_2}$. *The rates of change of the three concentrations are related by their stoichiometric factors, as shown by the different slopes of the tangents at t = 500 s.*

✓ Example 3.1.1: Expressions for Relative Reaction Rates

The first step in the production of nitric acid is the combustion of ammonia:

$$4\,\mathrm{NH_3}(g) + 5\,\mathrm{O_2}(g) \longrightarrow 4\,\mathrm{NO}(g) + 6\,\mathrm{H_2O}(g)$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Solution

Considering the stoichiometry of this homogeneous reaction, the rates for the consumption of reactants and formation of products are:

$$-\frac{1}{4}\frac{\Delta[\mathrm{NH_3}]}{\Delta t} = -\frac{1}{5}\frac{\Delta[\mathrm{O_2}]}{\Delta t} = \frac{1}{4}\frac{\Delta[\mathrm{NO}]}{\Delta t} = \frac{1}{6}\frac{\Delta[\mathrm{H_2O}]}{\Delta t}$$

? Exercise 3.1.1

The rate of formation of Br_2 is 6.0 × 10^{-6} mol/L/s in a reaction described by the following net ionic equation:

$$5\,\mathrm{Br^-} + \mathrm{BrO_3^-} + 6\,\mathrm{H^+} \longrightarrow 3\,\mathrm{Br_2} + 3\,\mathrm{H_2O}$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Answer

$$-\frac{1}{5}\frac{\Delta[\mathrm{Br^-}]}{\Delta t} = -\frac{\Delta[\mathrm{BrO_3^-}]}{\Delta t} = -\frac{1}{6}\frac{\Delta[\mathrm{H^+}]}{\Delta t} = \frac{1}{3}\frac{\Delta[\mathrm{Br_2}]}{\Delta t} = \frac{1}{3}\frac{\Delta[\mathrm{H_2O}]}{\Delta t}$$

✓ Example 3.1.2: Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure 3.1.4 shows the rate of the decomposition of H_2O_2 over time:

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

Based on these data, the instantaneous rate of decomposition of H_2O_2 at t = 11.1 h is determined to be 3.20 × 10^{-2} mol/L/h, that is:

$$-\frac{\Delta[H_2O_2]}{\Delta t} = 3.20 \times 10^{-2}\ \mathrm{mol\ L^{-1}\ h^{-1}}$$

What is the instantaneous rate of production of H_2O and O_2?

Solution

Using the stoichiometry of the reaction, we may determine that:

$$-\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Therefore:

$$\frac{1}{2} \times 3.20 \times 10^{-2}\ \mathrm{mol\ L^{-1}\ h^{-1}} = \frac{\Delta[O_2]}{\Delta t}$$

and

$$\frac{\Delta[O_2]}{\Delta t} = 1.60 \times 10^{-2}\ \mathrm{mol\ L^{-1}\ h^{-1}}$$

? Exercise 3.1.2

If the rate of decomposition of ammonia, NH_3, at 1150 K is 2.10 × 10^{-6} mol/L/s, what is the rate of production of nitrogen and hydrogen?

Answer

1.05 × 10^{-6} mol/L/s, N_2 and 3.15 × 10^{-6} mol/L/s, H_2.

Summary

The rate of a reaction can be expressed either in terms of the decrease in the amount of a reactant or the increase in the amount of a product per unit time. Relations between different rate expressions for a given reaction are derived directly from the stoichiometric coefficients of the equation representing the reaction.

Glossary

average rate

rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred

initial rate

instantaneous rate of a chemical reaction at t = 0 s (immediately after the reaction has begun)

instantaneous rate

rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time

rate of reaction

measure of the speed at which a chemical reaction takes place

rate expression

mathematical representation relating reaction rate to changes in amount, concentration, or pressure of reactant or product species per unit time

Contributors and Attributions

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3.2: Factors Affecting Reaction Rates

Learning Objectives

- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. We can identify five factors that affect the rates of chemical reactions: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

3.2.1: The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

3.2.2: The State of Subdivision of the Reactants

Except for substances in the gaseous state or in solution, reactions occur at the boundary, or interface, between two phases. Hence, the rate of a reaction between two phases depends to a great extent on the surface contact between them. A finely divided solid has more surface area available for reaction than does one large piece of the same substance. Thus a liquid will react more rapidly with a finely divided solid than with a large piece of the same solid. For example, large pieces of iron react slowly with acids; finely divided iron reacts much more rapidly (Figure $3.2.1$). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.

Figure $3.2.1$: (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas because the powder has a large total area.(b) An iron nail reacts more slowly.

$2Fe(s) + 6HCl(aq) \longrightarrow 2FeCl_3(aq) + 3H_2(g)$.

Video $\mathbf{3.2.1}$: *The reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.*

3.2.3: Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. In many cases, an increase in temperature of only 10 °C will approximately double the rate of a reaction in a homogeneous system.

3.2.4: Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate ($CaCO_3$) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (Figure $3.2.2$). As an acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$SO_{2(g)} + H_2O_{(g)} \longrightarrow H_2SO_{3(aq)} \tag{3.2.1}$$

Calcium carbonate reacts with sulfurous acid as follows:

$$CaCO_{3(s)} + H_2SO_{3(aq)} \longrightarrow CaSO_{3(aq)} + CO_{2(g)} + H_2O_{(l)} \tag{3.2.2}$$

In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.

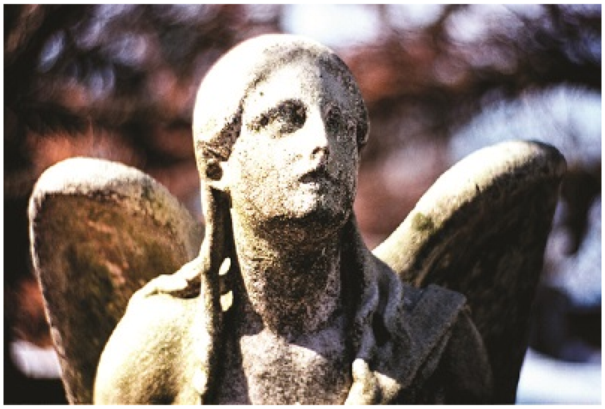

Figure $3.2.2$: Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III).

***Video $3.2.2$**: Phosphorus burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen in is higher.*

3.2.5: The Presence of a Catalyst

Hydrogen peroxide solutions foam when poured onto an open wound because substances in the exposed tissues act as catalysts, increasing the rate of hydrogen peroxide's decomposition. However, in the absence of these catalysts (for example, in the bottle in the medicine cabinet) complete decomposition can take months. A catalyst is a substance that increases the rate of a chemical reaction by lowering the activation energy without itself being consumed by the reaction. Activation energy is the minimum amount of energy required for a chemical reaction to proceed in the forward direction. A catalyst increases the reaction rate by providing an alternative pathway or mechanism for the reaction to follow (Figure $3.2.3$). Catalysis will be discussed in greater detail later in this chapter as it relates to mechanisms of reactions.

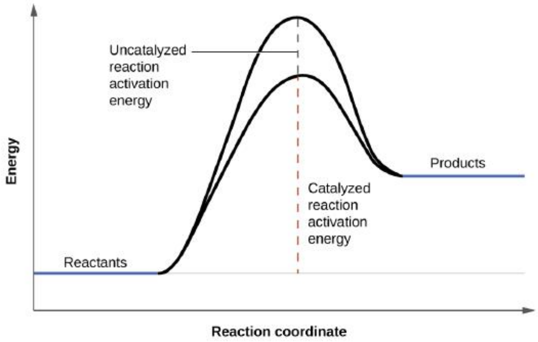

Figure $3.2.3$: The presence of a catalyst increases the rate of a reaction by lowering its activation energy.

> *Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the PhET Reactions & Rates interactive to explore how temperature, concentration, and the nature of the reactants affect reaction rates.*

Contributors and Attributions

Summary

The rate of a chemical reaction is affected by several parameters. Reactions involving two phases proceed more rapidly when there is greater surface area contact. If temperature or reactant concentration is increased, the rate of a given reaction generally increases as well. A catalyst can increase the rate of a reaction by providing an alternative pathway that causes the activation energy of the reaction to decrease.

Glossary

catalyst

substance that increases the rate of a reaction without itself being consumed by the reaction

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3.3: Rate Laws

Learning Objectives

- Explain the form and function of a rate law
- Use rate laws to calculate reaction rates
- Use rate and concentration data to identify reaction orders and derive rate laws

As described in the previous module, the rate of a reaction is affected by the concentrations of reactants. Rate laws or rate equations are mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants. In general, a rate law (or differential rate law, as it is sometimes called) takes this form:

$$\text{rate} = k[A]^m[B]^n[C]^p\ldots \tag{3.3.1}$$

in which $[A]$, $[B]$, and $[C]$ represent the molar concentrations of reactants, and k is the rate constant, which is specific for a particular reaction at a particular temperature. The exponents m, n, and p are usually positive integers (although it is possible for them to be fractions or negative numbers). The rate constant k and the exponents m, n, and p must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. The rate constant k is independent of the concentration of A, B, or C, but it does vary with temperature and surface area.

3.3.1: Writing Rate Laws

The exponents in a rate law describe the effects of the reactant concentrations on the reaction rate and define the reaction order. Consider a reaction for which the rate law is:

$$\text{rate} = k[A]^m[B]^n \tag{3.3.2}$$

If the exponent m is 1, the reaction is first order with respect to A. If m is 2, the reaction is second order with respect to A. If n is 1, the reaction is first order in B. If n is 2, the reaction is second order in B. If m or n is zero, the reaction is zero order in A or B, respectively, and the rate of the reaction is not affected by the concentration of that reactant. The overall reaction order is the sum of the orders with respect to each reactant. If $m = 1$ and $n = 1$, the overall order of the reaction is second order ($m + n = 1 + 1 = 2$).

The rate law:

$$\text{rate} = k[\text{H}_2\text{O}_2] \tag{3.3.3}$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate} = k[\text{C}_4\text{H}_6]^2 \tag{3.3.4}$$

describes a reaction that is second order in C_4H_6 and second order overall. The rate law:

$$\text{rate} = k[\text{H}^+][\text{OH}^-] \tag{3.3.5}$$

describes a reaction that is first order in H^+, first order in OH^-, and second order overall.

✓ Example 3.3.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\text{NO}_2(g) + \text{CO}(g) \longrightarrow \text{NO}(g) + \text{CO}_2(g)$$

is second order in NO_2 and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate} = k[\text{NO}_2]^m[\text{CO}]^n$$

The reaction is second order in NO_2; thus $m = 2$. The reaction is zero order in CO; thus $n = 0$. The rate law is:

$$\text{rate} = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of NO_2. When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

? Exercise $3.3.1A$

The rate law for the reaction:

$$\mathrm{H_2}(g) + 2\,\mathrm{NO}(g) \longrightarrow \mathrm{N_2O}(g) + \mathrm{H_2O}(g)$$

has been experimentally determined to be rate = $k[NO]^2[H_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer

- order in NO = 2;
- order in H_2 = 1;
- overall order = 3

? Exercise $3.3.1B$

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($CH_3CH_2OCOCH_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$\mathrm{CH_3OH} + \mathrm{CH_3CH_2OCOCH_3} \longrightarrow \mathrm{CH_3OCOCH_3} + \mathrm{CH_3CH_2OH}$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, experimentally determined to be:

$$\mathrm{rate} = k[\mathrm{CH_3OH}]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

- order in CH_3OH = 1;
- order in $CH_3CH_2OCOCH_3$ = 0;
- overall order = 1

3.3.2: Determining Reaction Order by the Initial Rates Method

It is sometimes helpful to use a more explicit algebraic method, often referred to as the method of initial rates, to determine the orders in rate laws. To use this method, we select two sets of rate data that differ in the concentration of only one reactant and set up a ratio of the two rates and the two rate laws. After canceling terms that are equal, we are left with an equation that contains only one unknown, the coefficient of the concentration that varies. We then solve this equation for the coefficient.

✓ Example 3.3.2: Determining a Rate Law from Initial Rates

Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica (Figure $3.3.1$). One such reaction is the combination of nitric oxide, NO, with ozone, O_3:

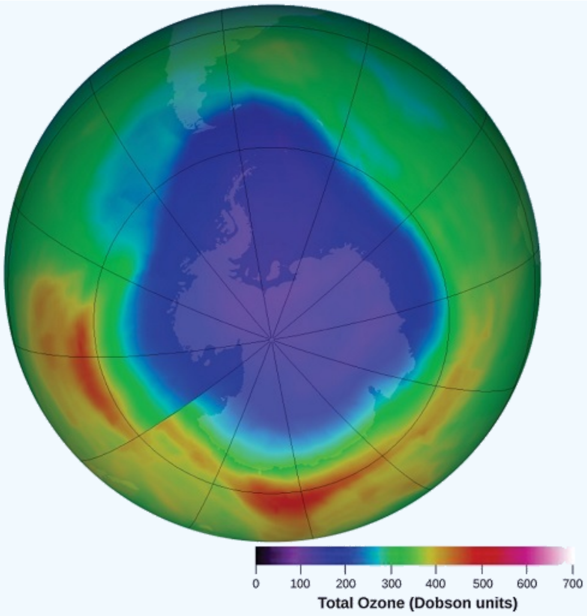

Figure 3.3.1: Over the past several years, the atmospheric ozone concentration over Antarctica has decreased during the winter. This map shows the decreased concentration as a purple area. (credit: modification of work by NASA)

$$\mathrm{NO}(g)+\mathrm{O_3}(g)\longrightarrow \mathrm{NO_2}(g)+\mathrm{O_2}(g)$$

This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	[NO] **(mol/L)**	$[\mathrm{O_3}]$ **(mol/L)**	$\frac{\Delta[\mathrm{NO_2}]}{\Delta t}$ $(\mathbf{mol\ L^{-1}\ s^{-1}})$
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
3	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
4	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
5	3.00×10^{-6}	9.00×10^{-6}	5.94×10^{-4}

Determine the rate law and the rate constant for the reaction at 25 °C.

Solution

The rate law will have the form:

$$\text{rate} = k[\mathrm{NO}]^m[\mathrm{O_3}]^n \tag{3.3.6}$$

We can determine the values of *m*, *n*, and *k* from the experimental data using the following three-part process:

1. *Determine the value of* m *from the data in which [NO] varies and [O$_3$] is constant.* In the last three experiments, [NO] varies while [O$_3$] remains constant. When [NO] doubles from trial 3 to 4, the rate doubles, and when [NO] triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to [NO], and *m* in the rate law is equal to 1.
2. *Determine the value of* n *from data in which [O$_3$] varies and [NO] is constant.* In the first three experiments, [NO] is constant and [O$_3$] varies. The reaction rate changes in direct proportion to the change in [O$_3$]. When [O$_3$] doubles from trial 1 to 2, the rate doubles; when [O$_3$] triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to [O$_3$], and *n* is equal to 1.The rate law is thus:

$$\text{rate} = k[\mathrm{NO}]^1[\mathrm{O_3}]^1 = k[\mathrm{NO}][\mathrm{O_3}] \tag{3.3.7}$$

3. *Determine the value of* k *from one set of concentrations and the corresponding rate.*

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{NO}][\text{O}_3]} \\ &= \frac{6.60\times10^{-5}\ \text{mol}\,\cancel{\text{L}^{-1}}\ \text{s}^{-1}}{(1.00\times10^{-6}\ \text{mol}\,\cancel{\text{L}^{-1}})(3.00\times10^{-6}\ \text{mol L}^{-1})} \\ &= 2.20\times10^{7}\ \text{L mol}^{-1}\ \text{s}^{-1} \end{aligned}$$

The large value of k tells us that this is a fast reaction that could play an important role in ozone depletion if [NO] is large enough.

Exercise 3.3.2

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

$$\text{CH}_3\text{CHO}(g) \longrightarrow \text{CH}_4(g) + \text{CO}(g) \tag{3.3.8}$$

Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	$[\text{CH}_3\text{CHO}]$ **(mol/L)**	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}$ $(\text{mol L}^{-1}\ \text{s}^{-1})$
1	1.75×10^{-3}	2.06×10^{-11}
2	3.50×10^{-3}	8.24×10^{-11}
3	7.00×10^{-3}	3.30×10^{-10}

Answer

$\text{rate} = k[\text{CH}_3\text{CHO}]^2$ with $k = 6.73 \times 10^{-6}$ L/mol/s

Example 3.3.3: Determining Rate Laws from Initial Rates

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:

$$2\,\text{NO}(g) + \text{Cl}_2(g) \longrightarrow 2\,\text{NOCl}(g) \tag{3.3.9}$$

Trial	[NO] (mol/L)	$[Cl_2]$ (mol/L)	$-\frac{\Delta[\text{NO}]}{2\Delta t}(\text{mol L}^{-1}\ \text{s}^{-1})$
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Solution

The rate law for this reaction will have the form:

$$\text{rate} = k[\text{NO}]^m[\text{Cl}_2]^n \tag{3.3.10}$$

As in Example $3.3.2$, we can approach this problem in a stepwise fashion, determining the values of m and n from the experimental data and then using these values to determine the value of k. In this example, however, we will use a different approach to determine the values of m and n:

Determine the value of m *from the data in which [NO] varies and* $[Cl_2]$ *is constant.* We can write the ratios with the subscripts x and y to indicate data from two different trials:

$$\frac{\text{rate}_x}{\text{rate}_y}=\frac{k[\text{NO}]_x^m[\text{Cl}_2]_x^n}{k[\text{NO}]_y^m[\text{Cl}_2]_y^n} \tag{3.3.11}$$

Using the third trial and the first trial, in which [Cl_2] does not vary, gives:

$$\frac{\text{rate 3}}{\text{rate 1}}=\frac{0.00675}{0.00300}=\frac{k(0.15)^m(0.10)^n}{k(0.10)^m(0.10)^n} \tag{3.3.12}$$

After canceling equivalent terms in the numerator and denominator, we are left with:

$$\frac{0.00675}{0.00300}=\frac{(0.15)^m}{(0.10)^m} \tag{3.3.13}$$

which simplifies to:

$$2.25=(1.5)^m \tag{3.3.14}$$

We can use natural logs to determine the value of the exponent *m*:

$$\ln(2.25)=m\ln(1.5)$$

$$\frac{\ln(2.25)}{\ln(1.5)}=m$$
$$2=m$$

We can confirm the result easily, since:

$$1.5^2=2.25$$

- *Determine the value of* n *from data in which [Cl_2] varies and [NO] is constant.*

  $$\frac{\text{rate 2}}{\text{rate 1}}=\frac{0.00450}{0.00300}=\frac{k(0.10)^m(0.15)^n}{k(0.10)^m(0.10)^n} \tag{3.3.15}$$

  Cancelation gives:

  $$\frac{0.0045}{0.0030}=\frac{(0.15)^n}{(0.10)^n} \tag{3.3.16}$$

  which simplifies to:

  $$1.5=(1.5)^n \tag{3.3.17}$$

  Thus *n* must be 1, and the form of the rate law is:

  $$\text{Rate}=k[\text{NO}]^m[\text{Cl}_2]^n=k[\text{NO}]^2[\text{Cl}_2] \tag{3.3.18}$$

- *Determine the numerical value of the rate constant* k *with appropriate units.* The units for the rate of a reaction are mol/L/s. The units for *k* are whatever is needed so that substituting into the rate law expression affords the appropriate units for the rate. In this example, the concentration units are mol^3/L^3. The units for *k* should be $\text{mol}^{-2}\ \text{L}^2/\text{s}$ so that the rate is in terms of mol/L/s.

  To determine the value of *k* once the rate law expression has been solved, simply plug in values from the first experimental trial and solve for *k*:

  $$0.00300\ \text{mol L}^{-1}\ \text{s}^{-1}=k(0.10\ \text{mol L}^{-1})^2(0.10\ \text{mol L}^{-1})^1$$
  $$k=3.0\ \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1}$$

? Exercise 3.3.3

Use the provided initial rate data to derive the rate law for the reaction whose equation is:

$$\text{OCl}^-(aq)+\text{I}^-(aq)\longrightarrow\text{OI}^-(aq)+\text{Cl}^-(aq) \tag{3.3.19}$$

Trial	$[OCl^-]$ (mol/L)	$[I^-]$ (mol/L)	Initial Rate (mol/L/s)
1	0.0040	0.0020	0.00184
2	0.0020	0.0040	0.00092
3	0.0020	0.0020	0.00046

Determine the rate law expression and the value of the rate constant *k* with appropriate units for this reaction.

Answer

$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{0.00092}{0.00046} = \frac{k(0.0020)^x(0.0040)^y}{k(0.0020)^x(0.0020)^y}$$

$$2.00 = 2.00^y$$

$$y = 1$$

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{0.00184}{0.00092} = \frac{k(0.0040)^x(0.0020)^y}{k(0.0020)^x(0.0040)^y}$$

$$\begin{aligned} 2.00 &= \frac{2^x}{2^y} \\ 2.00 &= \frac{2^x}{2^1} \\ 4.00 &= 2^x \\ x &= 2 \end{aligned}$$

Substituting the concentration data from trial 1 and solving for *k* yields:

$$\begin{aligned} \text{rate} &= k[\text{OCl}^-]^2[\text{I}^-]^1 \\ 0.00184 &= k(0.0040)^2(0.0020)^1 \\ k &= 5.75 \times 10^4 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1} \end{aligned}$$

3.3.3: Reaction Order and Rate Constant Units

In some of our examples, the reaction orders in the rate law happen to be the same as the coefficients in the chemical equation for the reaction. This is merely a coincidence and very often not the case. Rate laws may exhibit fractional orders for some reactants, and negative reaction orders are sometimes observed when an increase in the concentration of one reactant causes a decrease in reaction rate. A few examples illustrating these points are provided:

$$\begin{aligned} &\text{NO}_2 + \text{CO} \longrightarrow \text{NO} + \text{CO}_2 \quad \text{rate} = k[\text{NO}_2]^2 \\ &\text{CH}_3\text{CHO} \longrightarrow \text{CH}_4 + \text{CO} \quad \text{rate} = k[\text{CH}_3\text{CHO}]^2 \\ &2\,\text{N}_2\text{O}_5 \longrightarrow 2\,\text{NO}_2 + \text{O}_2 \quad \text{rate} = k[\text{N}_2\text{O}_5] \\ &2\,\text{NO}_2 + \text{F}_2 \longrightarrow 2\,\text{NO}_2\text{F} \quad \text{rate} = k[\text{NO}_2][\text{F}_2] \\ &2\,\text{NO}_2\text{Cl} \longrightarrow 2\,\text{NO}_2 + \text{Cl}_2 \quad \text{rate} = k[\text{NO}_2\text{Cl}] \end{aligned}$$

> *It is important to note that rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

Reaction orders also play a role in determining the units for the rate constant *k*. In Example $3.3.2$, a second-order reaction, we found the units for *k* to be $\text{L mol}^{-1}\text{ s}^{-1}$, whereas in Example $3.3.3$, a third order reaction, we found the units for *k* to be $\text{mol}^{-2}\text{ L}^2$/s. More generally speaking, the units for the rate constant for a reaction of order $(m+n)$ are $\text{mol}^{1-(m+n)}\text{L}^{(m+n)-1}\text{s}^{-1}$. Table $3.3.1$ summarizes the rate constant units for common reaction orders.

Table 3.3.1: Rate Constants for Common Reaction Orders

Reaction Order	Units of *k*
$(m+n)$	$\text{mol}^{1-(m+n)}\,\text{L}^{(m+n)-1}\,\text{s}^{-1}$

Reaction Order	Units of *k*
zero	mol/L/s
first	s^{-1}
second	L/mol/s
third	$mol^{-2}\ L^{2}\ s^{-1}$

Note that the units in the table can also be expressed in terms of molarity (*M*) instead of mol/L. Also, units of time other than the second (such as minutes, hours, days) may be used, depending on the situation.

Contributors and Attributions

Summary

Rate laws provide a mathematical description of how changes in the amount of a substance affect the rate of a chemical reaction. Rate laws are determined experimentally and cannot be predicted by reaction stoichiometry. The order of reaction describes how much a change in the amount of each substance affects the overall rate, and the overall order of a reaction is the sum of the orders for each substance present in the reaction. Reaction orders are typically first order, second order, or zero order, but fractional and even negative orders are possible.

Glossary

method of initial rates

use of a more explicit algebraic method to determine the orders in a rate law

overall reaction order

sum of the reaction orders for each substance represented in the rate law

rate constant (*k*)

proportionality constant in the relationship between reaction rate and concentrations of reactants

rate law

(also, rate equation) mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants

reaction order

value of an exponent in a rate law, expressed as an ordinal number (for example, zero order for 0, first order for 1, second order for 2, and so on)

Contributors and Attributions

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3.4: Integrated Rate Laws

Learning Objectives

- Explain the form and function of an integrated rate law
- Perform integrated rate law calculations for zero-, first-, and second-order reactions
- Define half-life and carry out related calculations
- Identify the order of a reaction from concentration/time data

The rate laws we have seen thus far relate the rate and the concentrations of reactants. We can also determine a second form of each rate law that relates the concentrations of reactants and time. These are called integrated rate laws. We can use an integrated rate law to determine the amount of reactant or product present after a period of time or to estimate the time required for a reaction to proceed to a certain extent. For example, an integrated rate law is used to determine the length of time a radioactive material must be stored for its radioactivity to decay to a safe level.

Using calculus, the differential rate law for a chemical reaction can be integrated with respect to time to give an equation that relates the amount of reactant or product present in a reaction mixture to the elapsed time of the reaction. This process can either be very straightforward or very complex, depending on the complexity of the differential rate law. For purposes of discussion, we will focus on the resulting integrated rate laws for first-, second-, and zero-order reactions.

3.4.1: First-Order Reactions

An equation relating the rate constant k to the initial concentration $[A]_0$ and the concentration $[A]_t$ present after any given time t can be derived for a first-order reaction and shown to be:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \tag{3.4.1}$$

or alternatively

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt \tag{3.4.2}$$

or

$$[A] = [A]_0 e^{-kt} \tag{3.4.3}$$

Example 3.4.1: The Integrated Rate Law for a First-Order Reaction

The rate constant for the first-order decomposition of cyclobutane, C_4H_8 at 500 °C is $9.2 \times 10^{-3}\ s^{-1}$:

$$C_4H_8 \longrightarrow 2\,C_2H_4 \tag{3.4.4}$$

How long will it take for 80.0% of a sample of C_4H_8 to decompose?

Solution

We use the integrated form of the rate law to answer questions regarding time:

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt \tag{3.4.5}$$

There are four variables in the rate law, so if we know three of them, we can determine the fourth. In this case we know $[A]_0$, $[A]$, and k, and need to find t.

The initial concentration of C_4H_8, $[A]_0$, is not provided, but the provision that 80.0% of the sample has decomposed is enough information to solve this problem. Let x be the initial concentration, in which case the concentration after 80.0% decomposition is 20.0% of x or $0.200x$. Rearranging the rate law to isolate t and substituting the provided quantities yields:

$$\begin{aligned} t &= \ln \frac{[x]}{[0.200x]} \times \frac{1}{k} \\ &= \ln \frac{1}{0.2} \times \frac{1}{9.2 \times 10^{-3}\ \mathrm{s}^{-1}} \\ &= 1.609 \times \frac{1}{9.2 \times 10^{-3}\ \mathrm{s}^{-1}} \\ &= 1.7 \times 10^{2}\ \mathrm{s} \end{aligned}$$

? Exercise 3.4.1

Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131 according to the equation:

$$\text{I-131} \longrightarrow \text{Xe-131} + \text{electron} \tag{3.4.6}$$

The decay is first-order with a rate constant of 0.138 d^{-1}. How many days will it take for 90% of the iodine−131 in a 0.500 M solution of this substance to decay to Xe-131?

Answer

16.7 days

We can use integrated rate laws with experimental data that consist of time and concentration information to determine the order and rate constant of a reaction. The integrated rate law can be rearranged to a standard linear equation format:

$$\ln[A] = (-k)(t) + \ln[A]_0 \tag{3.4.7}$$

$$y = mx + b \tag{3.4.8}$$

A plot of $\ln[A]$ versus t for a first-order reaction is a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$. If a set of rate data are plotted in this fashion but do *not* result in a straight line, the reaction is not first order in A.

✓ Example 3.4.2: Determination of Reaction Order by Graphing

Show that the data in this Figure can be represented by a first-order rate law by graphing $\ln[H_2O_2]$ versus time. Determine the rate constant for the rate of decomposition of H_2O_2 from this data.

Solution

The data from this Figure with the addition of values of $\ln[H_2O_2]$ are given in Figure 3.4.1.

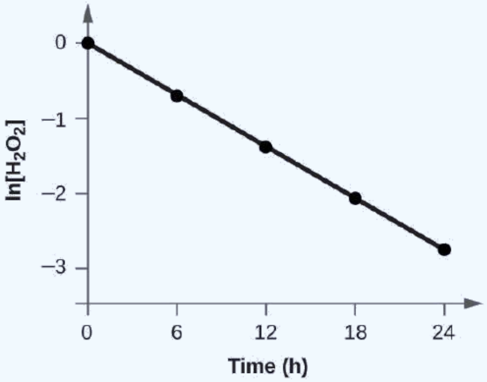


Figure 3.4.1: The linear relationship between the $\ln[H_2O_2]$ and time shows that the decomposition of hydrogen peroxide is a first-order reaction.

Trial	Time (h)	$[H_2O_2]$ (M)	$\ln[H_2O_2]$
1	0	1.000	0.0

Trial	Time (h)	$[H_2O_2]$ (M)	$\ln[H_2O_2]$
2	6.00	0.500	−0.693
3	12.00	0.250	−1.386
4	18.00	0.125	−2.079
5	24.00	0.0625	−2.772

The plot of $\ln[H_2O_2]$ versus time is linear, thus we have verified that the reaction may be described by a first-order rate law.

The rate constant for a first-order reaction is equal to the negative of the slope of the plot of $\ln[H_2O_2]$ versus time where:

$$\text{slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln[H_2O_2]}{\Delta t} \tag{3.4.9}$$

In order to determine the slope of the line, we need two values of $\ln[H_2O_2]$ at different values of t (one near each end of the line is preferable). For example, the value of $\ln[H_2O_2]$ when t is 6.00 h is −0.693; the value when t = 12.00 h is −1.386:

$$\begin{aligned} \text{slope} &= \frac{-1.386-(-0.693)}{12.00\text{ h}-6.00\text{ h}} \\ &= \frac{-0.693}{6.00\text{ h}} \\ &= -1.155\times 10^{-2}\text{ h}^{-1} \\ k\ &= -\text{slope} = -(-1.155\times 10^{-1}\text{ h}^{-1}) = 1.155\times 10^{-1}\text{ h}^{-1} \end{aligned}$$

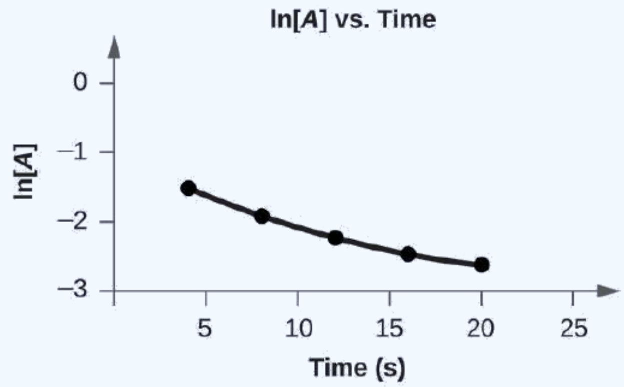
Exercise 3.4.2

Graph the following data to determine whether the reaction $A \longrightarrow B+C$ is first order.

Trial	Time (s)	[A]
1	4.0	0.220
2	8.0	0.144
3	12.0	0.110
4	16.0	0.088
5	20.0	0.074

Answer

The plot of ln[A] vs. t is not a straight line. The equation is not first order:



3.4.2: Second-Order Reactions

The equations that relate the concentrations of reactants and the rate constant of second-order reactions are fairly complicated. We will limit ourselves to the simplest second-order reactions, namely, those with rates that are dependent upon just one reactant's concentration and described by the differential rate law:

$$\text{Rate} = k[A]^2 \tag{3.4.10}$$

For these second-order reactions, the integrated rate law is:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \tag{3.4.11}$$

where the terms in the equation have their usual meanings as defined earlier.

✓ Example 3.4.3: The Integrated Rate Law for a Second-Order Reaction

The reaction of butadiene gas (C_4H_6) with itself produces C_8H_{12} gas as follows:

$$2\,C_4H_6(g) \longrightarrow C_8H_{12}(g) \tag{3.4.12}$$

The reaction is second order with a rate constant equal to 5.76 × 10^{-2} L/mol/min under certain conditions. If the initial concentration of butadiene is 0.200 *M*, what is the concentration remaining after 10.0 min?

Solution

We use the integrated form of the rate law to answer questions regarding time. For a second-order reaction, we have:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \tag{3.4.13}$$

We know three variables in this equation: $[A]_0$ = 0.200 mol/L, k = 5.76 × 10^{-2} L/mol/min, and t = 10.0 min. Therefore, we can solve for [*A*], the fourth variable:

$$\begin{aligned} \frac{1}{[A]} &= (5.76 \times 10^{-2}\ \text{L mol}^{-1}\ \text{min}^{-1})(10\ \text{min}) + \frac{1}{0.200\ \text{mol L}^{-1}} \\ \frac{1}{[A]} &= (5.76 \times 10^{-1}\ \text{L mol}^{-1}) + 5.00\ \text{L mol}^{-1} \\ \frac{1}{[A]} &= 5.58\ \text{L mol}^{-1} \\ [A] &= 1.79 \times 10^{-1}\ \text{mol L}^{-1} \end{aligned}$$

Therefore 0.179 mol/L of butadiene remain at the end of 10.0 min, compared to the 0.200 mol/L that was originally present.

? Exercise 3.4.3

If the initial concentration of butadiene is 0.0200 *M*, what is the concentration remaining after 20.0 min?

Answer

0.0196 mol/L

The integrated rate law for our second-order reactions has the form of the equation of a straight line:

$$\begin{gathered} \frac{1}{[A]} = kt + \frac{1}{[A]_0} \\ y = mx + b \end{gathered}$$

A plot of $\frac{1}{[A]}$ versus t for a second-order reaction is a straight line with a slope of k and an intercept of $\frac{1}{[A]_0}$. If the plot is not a straight line, then the reaction is not second order.

Example 3.4.4: Determination of Reaction Order by Graphing

Test the data given to show whether the dimerization of C_4H_6 is a first- or a second-order reaction.

Solution

Trial	Time (s)	$[C_4H_6]$ (M)
1	0	1.00×10^{-2}
2	1600	5.04×10^{-3}
3	3200	3.37×10^{-3}
4	4800	2.53×10^{-3}
5	6200	2.08×10^{-3}

In order to distinguish a first-order reaction from a second-order reaction, we plot $\ln[C_4H_6]$ versus t and compare it with a plot of $\frac{1}{[C_4H_6]}$ versus t. The values needed for these plots follow.

Time (s)	$\frac{1}{[C_4H_6]}$ (M^{-1})	$\ln[C_4H_6]$
0	100	−4.605
1600	198	−5.289
3200	296	−5.692
4800	395	−5.978
6200	481	−6.175

The plots are shown in Figure 3.4.2. As you can see, the plot of $\ln[C_4H_6]$ versus t is not linear, therefore the reaction is not first order. The plot of $\frac{1}{[C_4H_6]}$ versus t is linear, indicating that the reaction is second order.

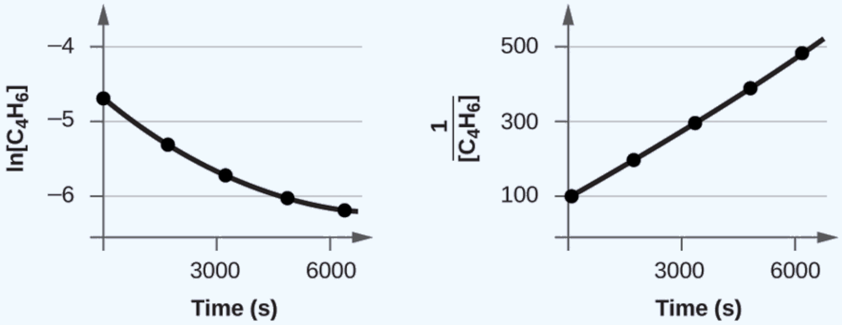


Figure 3.4.2: These two graphs show first- and second-order plots for the dimerization of C_4H_6. Since the first-order plot (left) is not linear, we know that the reaction is not first order. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

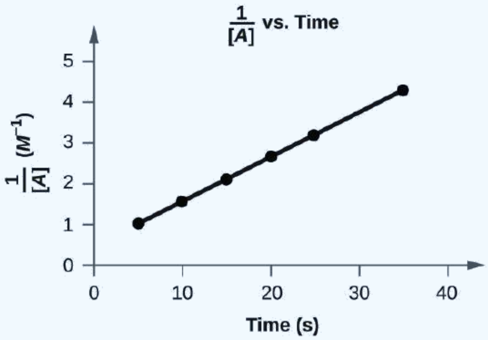
Exercise 3.4.4

Does the following data fit a second-order rate law?

Trial	Time (s)	[*A*] (*M*)
1	5	0.952
2	10	0.625
3	15	0.465
4	20	0.370
5	25	0.308
6	35	0.230

Answer

Yes. The plot of $\frac{1}{[A]}$ vs. *t* is linear:



3.4.3: Zero-Order Reactions

For zero-order reactions, the differential rate law is:

$$\text{Rate} = k[A]^0 = k \tag{3.4.14}$$

A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactants.

The integrated rate law for a zero-order reaction also has the form of the equation of a straight line:

$$\begin{aligned} [A] &= -kt + [A]_0 \\ y &= mx + b \end{aligned}$$

A plot of $[A]$ versus t for a zero-order reaction is a straight line with a slope of $-k$ and an intercept of $[A]_0$. Figure 3.4.3 shows a plot of $[NH_3]$ versus *t* for the decomposition of ammonia on a hot tungsten wire and for the decomposition of ammonia on hot quartz (SiO_2). The decomposition of NH_3 on hot tungsten is zero order; the plot is a straight line. The decomposition of NH_3 on hot quartz is not zero order (it is first order). From the slope of the line for the zero-order decomposition, we can determine the rate constant:

$$\text{slope} = -k = 1.3110^{-6}\ \text{mol/L/s} \tag{3.4.15}$$

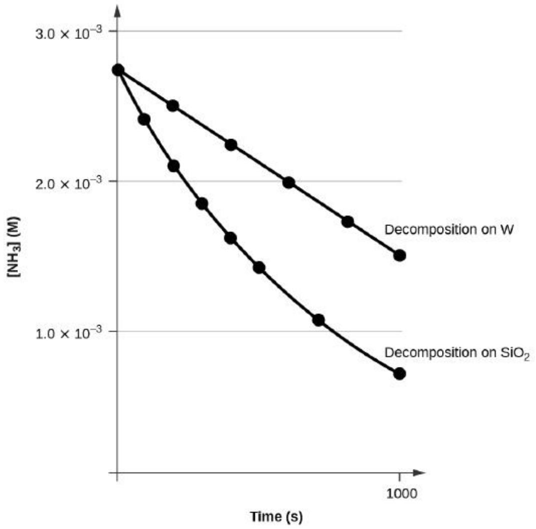


Figure 3.4.3: The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.

3.4.4: The Half-Life of a Reaction

The half-life of a reaction ($t_{1/2}$) is the time required for one-half of a given amount of reactant to be consumed. In each succeeding half-life, half of the remaining concentration of the reactant is consumed. Using the decomposition of hydrogen peroxide as an example, we find that during the first half-life (from 0.00 hours to 6.00 hours), the concentration of H_2O_2 decreases from 1.000 *M* to 0.500 *M*. During the second half-life (from 6.00 hours to 12.00 hours), it decreases from 0.500 *M* to 0.250 *M*; during the third half-life, it decreases from 0.250 *M* to 0.125 *M*. The concentration of H_2O_2 decreases by half during each successive period of 6.00 hours. The decomposition of hydrogen peroxide is a first-order reaction, and, as can be shown, the half-life of a first-order reaction is independent of the concentration of the reactant. However, half-lives of reactions with other orders depend on the concentrations of the reactants.

3.4.4.1: First-Order Reactions

We can derive an equation for determining the half-life of a first-order reaction from the alternate form of the integrated rate law as follows:

$$\ln \frac{[A]_0}{[A]} = kt$$

$$t = \ln \frac{[A]_0}{[A]} \times \frac{1}{k}$$

If we set the time t equal to the half-life, $t_{1/2}$, the corresponding concentration of A at this time is equal to one-half of its initial concentration. Hence, when $t = t_{1/2}$, $[A] = \frac{1}{2}[A]_0$.

Therefore:

$$t_{1/2} = \ln \frac{[A]_0}{\frac{1}{2}[A]_0} \times \frac{1}{k}$$

$$= \ln 2 \times \frac{1}{k} = 0.693 \times \frac{1}{k}$$

Thus:

$$t_{1/2} = \frac{0.693}{k} \tag{3.4.16}$$

We can see that the half-life of a first-order reaction is inversely proportional to the rate constant *k*. A fast reaction (shorter half-life) will have a larger *k*; a slow reaction (longer half-life) will have a smaller *k*.

✓ Example 3.4.5: Calculation of a First-order Rate Constant using Half-Life

Calculate the rate constant for the first-order decomposition of hydrogen peroxide in water at 40 °C, using the data given in Figure 3.4.4.

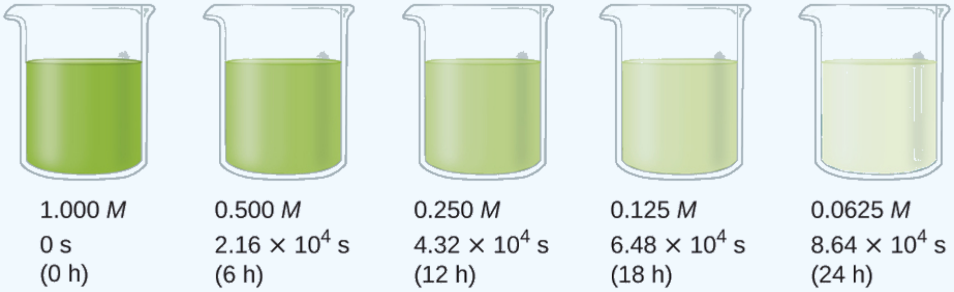


Figure 3.4.4: The decomposition of H_2O_2 $(2\,H_2O_2 \longrightarrow 2\,H_2O + O_2)$ *at 40 °C is illustrated. The intensity of the color symbolizes the concentration of* H_2O_2 *at the indicated times;* H_2O_2 *is actually colorless.*

Solution The half-life for the decomposition of H_2O_2 is 2.16×10^4 s:

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.16 \times 10^4\ \text{s}} = 3.21 \times 10^{-5}\ \text{s}^{-1}$$

? Exercise 3.4.1

The first-order radioactive decay of iodine-131 exhibits a rate constant of 0.138 d^{-1}. What is the half-life for this decay?

Answer

5.02 d.

3.4.4.2: Second-Order Reactions

We can derive the equation for calculating the half-life of a second order as follows:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \tag{3.4.17}$$

or

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt \tag{3.4.18}$$

If

$$t = t_{1/2} \tag{3.4.19}$$

then

$$[A] = \frac{1}{2}[A]_0 \tag{3.4.20}$$

and we can write:

$$\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$2[A]_0 - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{1}{[A]_0} = kt_{1/2}$$

Thus:

$$t_{1/2} = \frac{1}{k[A]_0} \tag{3.4.21}$$

For a second-order reaction, $t_{1/2}$ is inversely proportional to the concentration of the reactant, and the half-life increases as the reaction proceeds because the concentration of reactant decreases. Consequently, we find the use of the half-life concept to be more complex for second-order reactions than for first-order reactions. Unlike with first-order reactions, the rate constant of a second-order reaction cannot be calculated directly from the half-life unless the initial concentration is known.

3.4.4.3: Zero-Order Reactions

We can derive an equation for calculating the half-life of a zero order reaction as follows:

$$[A] = -kt + [A]_0 \tag{3.4.22}$$

When half of the initial amount of reactant has been consumed $t = t_{1/2}$ and $[A] = \frac{[A]_0}{2}$. Thus:

$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

$$kt_{1/2} = \frac{[A]_0}{2}$$

and

$$t_{1/2} = \frac{[A]_0}{2k} \tag{3.4.23}$$

The half-life of a zero-order reaction increases as the initial concentration increases. Equations for both differential and integrated rate laws and the corresponding half-lives for zero-, first-, and second-order reactions are summarized in Table $3.4.1$.

Table $3.4.1$: Summary of Rate Laws for Zero-, First-, and Second-Order Reactions

	Zero-Order	**First-Order**	**Second-Order**
rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
units of rate constant	$M\ s^{-1}$	s^{-1}	$M^{-1}\ s^{-1}$
integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \left(\frac{1}{[A]_0}\right)$
plot needed for linear fit of rate data	$[A]$ vs. t	$\ln[A]$ vs. t	$\frac{1}{[A]}$ vs. t
relationship between slope of linear plot and rate constant	k = −slope	k = −slope	k = +slope
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

Contributors and Attributions

Summary

Differential rate laws can be determined by the method of initial rates or other methods. We measure values for the initial rates of a reaction at different concentrations of the reactants. From these measurements, we determine the order of the reaction in each reactant. Integrated rate laws are determined by integration of the corresponding differential rate laws. Rate constants for those rate laws are determined from measurements of concentration at various times during a reaction.

The half-life of a reaction is the time required to decrease the amount of a given reactant by one-half. The half-life of a zero-order reaction decreases as the initial concentration of the reactant in the reaction decreases. The half-life of a first-order reaction is independent of concentration, and the half-life of a second-order reaction decreases as the concentration increases.

3.4.5: Key Equations

- integrated rate law for zero-order reactions (Equation ???):

$$[A] = -kt + [A]_0 \quad \text{with } t_{1/2} = \frac{[A]_0}{2k}$$

- integrated rate law for first-order reactions (Equation 3.4.7):

$$\ln[A] = -kt + \ln[A]_0 \quad \text{with } t_{1/2} = \frac{0.693}{k}$$

- integrated rate law for second-order reactions (Equation 3.4.11):

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \quad \text{with } t_{1/2} = \frac{1}{[A]_0 k}$$

Glossary

half-life of a reaction ($t_{1/2}$)

time required for half of a given amount of reactant to be consumed

integrated rate law

equation that relates the concentration of a reactant to elapsed time of reaction

Contributors and Attributions

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3.5: Collision Theory

Learning Objectives

- Use the postulates of collision theory to explain the effects of physical state, temperature, and concentration on reaction rates
- Define the concepts of activation energy and transition state
- Use the Arrhenius equation in calculations relating rate constants to temperature

We should not be surprised that atoms, molecules, or ions must collide before they can react with each other. Atoms must be close together to form chemical bonds. This simple premise is the basis for a very powerful theory that explains many observations regarding chemical kinetics, including factors affecting reaction rates. Collision theory is based on the following postulates:

Postulates of Collision theory

1. The rate of a reaction is proportional to the rate of reactant collisions:

$$\text{reaction rate} \propto \frac{\#\,\text{collisions}}{\text{time}}$$

2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

We can see the importance of the two physical factors noted in postulates 2 and 3, the orientation and energy of collisions, when we consider the reaction of carbon monoxide with oxygen:

$$2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$$

Carbon monoxide is a pollutant produced by the combustion of hydrocarbon fuels. To reduce this pollutant, automobiles have catalytic converters that use a catalyst to carry out this reaction. It is also a side reaction of the combustion of gunpowder that results in muzzle flash for many firearms. If carbon monoxide and oxygen are present in sufficient quantity, the reaction is spontaneous at high temperature and pressure.

The first step in the gas-phase reaction between carbon monoxide and oxygen is a collision between the two molecules:

$$CO(g) + O_2(g) \longrightarrow CO_2(g) + O(g)$$

Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in Figure $3.5.1$. In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms $(O=C=O)$. This is a rather simple example of how important the orientation of the collision is in terms of creating the desired product of the reaction.

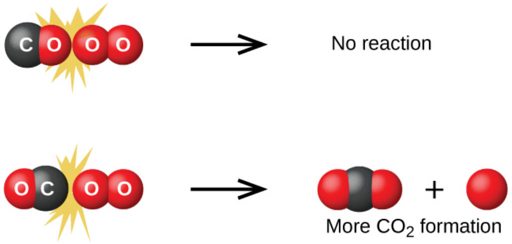

Figure $3.5.1$: Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. Every reaction requires a certain amount of activation energy for it to proceed in the forward direction, yielding an appropriate activated complex along the way. As Figure $3.5.2$ demonstrates, even a collision with the correct orientation can fail to form the reaction product. In the study of reaction mechanisms, each of these three arrangements of atoms is called a proposed activated complex or transition state.

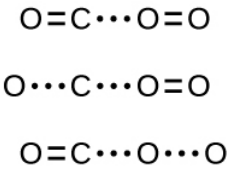

Figure $3.5.2$: Possible transition states (activated complexes) for carbon monoxide reacting with oxygen to form carbon dioxide. Solid lines represent covalent bonds, while dotted lines represent unstable orbital overlaps that may, or may not, become covalent bonds as product is formed. In the first two examples in this figure, the O=O double bond is not impacted; therefore, carbon dioxide cannot form. The third proposed transition state will result in the formation of carbon dioxide if the third “extra” oxygen atom separates from the rest of the molecule.

In most circumstances, it is impossible to isolate or identify a transition state or activated complex. In the reaction between carbon monoxide and oxygen to form carbon dioxide, activated complexes have only been observed spectroscopically in systems that utilize a heterogeneous catalyst. The gas-phase reaction occurs too rapidly to isolate any such chemical compound.

Collision theory explains why most reaction rates increase as concentrations increase. With an increase in the concentration of any reacting substance, the chances for collisions between molecules are increased because there are more molecules per unit of volume. More collisions mean a faster reaction rate, assuming the energy of the collisions is adequate.

3.5.1: Activation Energy and the Arrhenius Equation

The minimum energy necessary to form a product during a collision between reactants is called the activation energy (E_a). The kinetic energy of reactant molecules plays an important role in a reaction because the energy necessary to form a product is provided by a collision of a reactant molecule with another reactant molecule. (In single-reactant reactions, activation energy may be provided by a collision of the reactant molecule with the wall of the reaction vessel or with molecules of an inert contaminant.) If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly: Only a few fast-moving molecules will have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules, the fraction of molecules possessing the necessary kinetic energy will be large; most collisions between molecules will result in reaction, and the reaction will occur rapidly.

Figure $3.5.3$ shows the energy relationships for the general reaction of a molecule of A with a molecule of B to form molecules of C and D:

$$A+B\longrightarrow C+D$$

The figure shows that the energy of the transition state is higher than that of the reactants A and B by an amount equal to E_a, the activation energy. Thus, the sum of the kinetic energies of A and B must be **equal to or greater** than E_a to reach the transition state. After the transition state has been reached, and as C and D begin to form, the system loses energy until its total energy is lower than that of the initial mixture. This lost energy is transferred to other molecules, giving them enough energy to reach the transition state. The forward reaction (that between molecules A and B) therefore tends to take place readily once the reaction has started. In Figure $3.5.3$, ΔH represents the difference in enthalpy between the reactants (A and B) and the products (C and D). The sum of E_a and ΔH represents the activation energy for the reverse reaction:

$$C+D\longrightarrow A+B$$

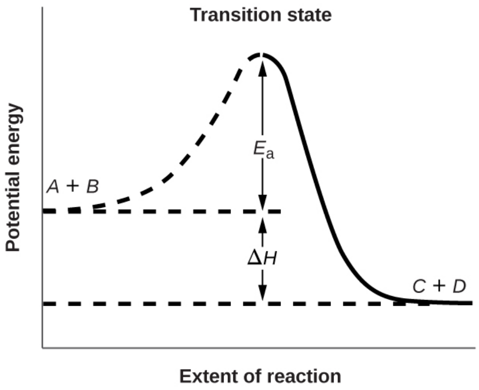

Figure 3.5.3: This graph shows the potential energy relationships for the reaction $A+B \longrightarrow C+D$. The dashed portion of the curve represents the energy of the system with a molecule of A and a molecule of B present, and the solid portion the energy of the system with a molecule of C and a molecule of D present. The activation energy for the forward reaction is represented by E_a. The activation energy for the reverse reaction is greater than that for the forward reaction by an amount equal to ΔH. The curve's peak represents the transition state.

We can use the Arrhenius equation to relate the activation energy and the rate constant, *k*, of a given reaction:

$$k=Ae^{-E_a/RT} \tag{3.5.1}$$

In this equation,

- R is the ideal gas constant, which has a value 8.314 J/mol/K,
- T is temperature on the Kelvin scale,
- E_a is the activation energy in joules per mole,
- e is the constant 2.7183, and
- A is a constant called the frequency factor, which is related to the frequency of collisions and the orientation of the reacting molecules.

Both postulates of the collision theory of reaction rates are accommodated in the Arrhenius equation. The frequency factor *A* is related to the rate at which collisions having the correct *orientation* occur. The exponential term, $e^{-E_a/RT}$, is related to the fraction of collisions providing adequate *energy* to overcome the activation barrier of the reaction.

At one extreme, the system does not contain enough energy for collisions to overcome the activation barrier. In such cases, no reaction occurs. At the other extreme, the system has so much energy that every collision with the correct orientation can overcome the activation barrier, causing the reaction to proceed. In such cases, the reaction is nearly instantaneous.

The Arrhenius equation (Equation 3.5.1) describes quantitatively much of what we have already discussed about reaction rates. For two reactions at the same temperature, the reaction with the higher activation energy has the lower rate constant and the slower rate. The larger value of E_a results in a smaller value for $e^{-E_a/RT}$, reflecting the smaller fraction of molecules with enough energy to react. Alternatively, the reaction with the smaller E_a has a larger fraction of molecules with enough energy to react. This will be reflected as a larger value of $e^{-E_a/RT}$, a larger rate constant, and a faster rate for the reaction.

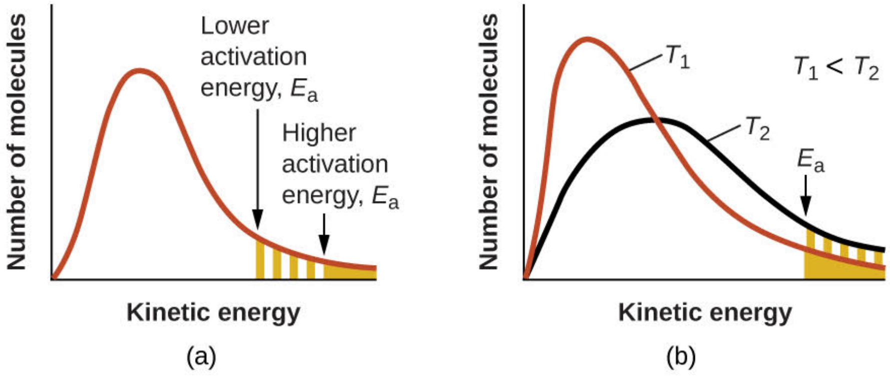

Figure 3.5.4: (a) As the activation energy of a reaction decreases, the number of molecules with at least this much energy increases, as shown by the shaded areas. (b) At a higher temperature, T2, more molecules have kinetic energies greater than Ea, as shown by the yellow shaded area.

An increase in temperature has the same effect as a decrease in activation energy. A larger fraction of molecules has the necessary energy to react (Figure 3.5.4), as indicated by an increase in the value of $e^{-E_a/RT}$. The rate constant is also directly proportional to the frequency factor, A. Hence a change in conditions or reactants that increases the number of collisions with a favorable orientation for reaction results in an increase in A and, consequently, an increase in k.

A convenient approach to determining E_a for a reaction involves the measurement of k at different temperatures and using of an alternate version of the Arrhenius equation that takes the form of linear equation:

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$
$$y = mx + b$$

Thus, a plot of $\ln k$ versus $\frac{1}{T}$ gives a straight line with the slope $\frac{-E_a}{R}$, from which E_a may be determined. The intercept gives the value of $\ln A$. This is sometimes call an Arrhenius Plot.

✓ Example 3.5.1

Determination of E_a The variation of the rate constant with temperature for the decomposition of HI(g) to H_2(g) and I_2(g) is given here. What is the activation energy for the reaction?

$$2\,\mathrm{HI}(g) \longrightarrow \mathrm{H_2}(g) + \mathrm{I_2}(g)$$

variation of the rate constant with temperature for the decomposition of HI(g) to H2(g) and I2(g)

T **(K)**	***k*** **(L/mol/s)**
555	3.52×10^{-7}
575	1.22×10^{-6}
645	8.59×10^{-5}
700	1.16×10^{-3}
781	3.95×10^{-2}

Solution

Values of $\frac{1}{T}$ and ln k are:

Solutions to Example 12.5.1

$\frac{1}{\mathbf{T}}\ (\mathbf{K}^{-1})$	**ln *k***

$\frac{1}{T}$ (K^{-1})	ln *k*
1.80×10^{-3}	−14.860
1.74×10^{-3}	−13.617
1.55×10^{-3}	−9.362
1.43×10^{-3}	−6.759
1.28×10^{-3}	−3.231

Figure $3.5.5$ is a graph of ln *k* versus $\frac{1}{T}$. To determine the slope of the line, we need two values of ln *k*, which are determined from the line at two values of $\frac{1}{T}$ (one near each end of the line is preferable). For example, the value of ln *k* determined from the line when $\frac{1}{T} = 1.25 \times 10^{-3}$ is −2.593; the value when $\frac{1}{T} = 1.78 \times 10^{-3}$ is −14.447.

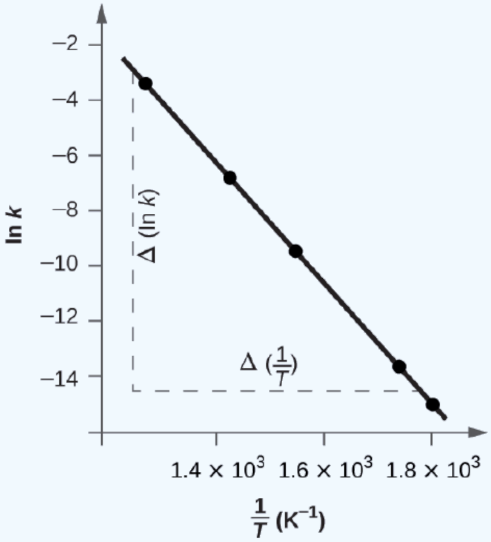

Figure $3.5.5$: This graph shows the linear relationship between ln *k* and $\frac{1}{T}$ for the reaction $2\,\mathrm{HI} \longrightarrow \mathrm{H_2} + \mathrm{I_2}$ according to the Arrhenius equation.

The slope of this line is given by the following expression:

$$\begin{aligned} \text{Slope} &= \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} \\ &= \frac{(-14.447) - (-2.593)}{(1.78 \times 10^{-3}\ \mathrm{K^{-1}}) - (1.25 \times 10^{-3}\ \mathrm{K^{-1}})} \\ &= \frac{-11.854}{0.53 \times 10^{-3}\ \mathrm{K^{-1}}} = 2.2 \times 10^{4}\ \mathrm{K} \\ &= -\frac{E_a}{R} \end{aligned}$$

Thus:

$$\begin{aligned} E_a &= -\text{slope} \times R = -(-2.2 \times 10^{4}\ \mathrm{K} \times 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}) \\ &= 1.8 \times 10^{5}\ \mathrm{J\ mol^{-1}} \end{aligned}$$

In many situations, it is possible to obtain a reasonable estimate of the activation energy without going through the entire process of constructing the Arrhenius plot. The Arrhenius equation:

$$\ln k=\left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right)+\ln A$$

can be rearranged as shown to give:

$$\frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)}=-\frac{E_a}{R}$$

or

$$\ln\frac{k_1}{k_2}=\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

This equation can be rearranged to give a one-step calculation to obtain an estimate for the activation energy:

$$E_a=-R\left(\frac{\ln k_2-\ln k_1}{\left(\frac{1}{T_2}\right)-\left(\frac{1}{T_1}\right)}\right)$$

Using the experimental data presented here, we can simply select two data entries. For this example, we select the first entry and the last entry:

First and Last Entry

T (K)	k (L/mol/s)	$\frac{1}{T}$ (K^{-1})	ln k
555	3.52×10^{-7}	1.80×10^{-3}	−14.860
781	3.95×10^{-2}	1.28×10^{-3}	−3.231

After calculating $\frac{1}{T}$ and ln k, we can substitute into the equation:

$$E_a=-8.314\text{ J mol}^{-1}\text{ K}^{-1}\left(\frac{-3.231-(-14.860)}{1.28\times10^{-3}\text{ K}^{-1}-1.80\times10^{-3}\text{ K}^{-1}}\right)$$

and the result is E_a = 185,900 J/mol.

This method is very effective, especially when a limited number of temperature-dependent rate constants are available for the reaction of interest.

? Exercise 3.5.1

The rate constant for the rate of decomposition of N_2O_5 to NO and O_2 in the gas phase is 1.66 L/mol/s at 650 K and 7.39 L/mol/s at 700 K:

$$2\,N_2O_5(g)\longrightarrow 4\,NO(g)+3\,O_2(g)$$

Assuming the kinetics of this reaction are consistent with the Arrhenius equation, calculate the activation energy for this decomposition.

Answer

113,000 J/mol

Summary

Chemical reactions require collisions between reactant species. These reactant collisions must be of proper orientation and sufficient energy in order to result in product formation. Collision theory provides a simple but effective explanation for the effect of many experimental parameters on reaction rates. The Arrhenius equation describes the relation between a reaction's rate constant and its activation energy, temperature, and dependence on collision orientation.

3.5.2: Key Equations

- $k = Ae^{-E_a/RT}$
- $\ln k = \left(\frac{-E_\text{a}}{R}\right)\left(\frac{1}{T}\right) + \ln A$
- $\ln \frac{k_1}{k_2} = \frac{E_\text{a}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Glossary

activated complex

(also, transition state) unstable combination of reactant species representing the highest energy state of a reaction system

activation energy (E_a)

energy necessary in order for a reaction to take place

Arrhenius equation

mathematical relationship between the rate constant and the activation energy of a reaction

collision theory

model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics

frequency factor (A)

proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation

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3.6: Reaction Mechanisms

Learning Objectives

- Distinguish net reactions from elementary reactions (steps)
- Identify the molecularity of elementary reactions
- Write a balanced chemical equation for a process given its reaction mechanism
- Derive the rate law consistent with a given reaction mechanism

A balanced equation for a chemical reaction indicates what is reacting and what is produced, but it reveals nothing about how the reaction actually takes place. The reaction mechanism (or reaction path) is the process, or pathway, by which a reaction occurs. A chemical reaction often occurs in steps, although it may not always be obvious to an observer. The decomposition of ozone, for example, appears to follow a mechanism with two steps:

$$\begin{gathered} O_3(g) \longrightarrow O_2(g) + O \\ O + O_3(g) \longrightarrow 2\,O_2(g) \end{gathered} \tag{3.6.1}$$

We call each step in a reaction mechanism an elementary reaction. Elementary reactions occur exactly as they are written and cannot be broken down into simpler steps. Elementary reactions add up to the overall reaction, which, for the decomposition, is:

$$2\,O_3(g) \longrightarrow 3\,O_2(g) \tag{3.6.2}$$

Notice that the oxygen atom produced in the first step of this mechanism is consumed in the second step and therefore does not appear as a product in the overall reaction. Species that are produced in one step and consumed in a subsequent step are called intermediates.

While the overall reaction equation for the decomposition of ozone indicates that two molecules of ozone react to give three molecules of oxygen, the mechanism of the reaction does not involve the collision and reaction of two ozone molecules. Rather, it involves a molecule of ozone decomposing to an oxygen molecule and an intermediate oxygen atom; the oxygen atom then reacts with a second ozone molecule to give two oxygen molecules. These two elementary reactions occur exactly as they are shown in the reaction mechanism.

3.6.1: Unimolecular Elementary Reactions

The molecularity of an elementary reaction is the number of reactant species (atoms, molecules, or ions). For example, a unimolecular reaction involves the rearrangement of a *single* reactant species to produce one or more molecules of product:

$$A \longrightarrow \text{products} \tag{3.6.3}$$

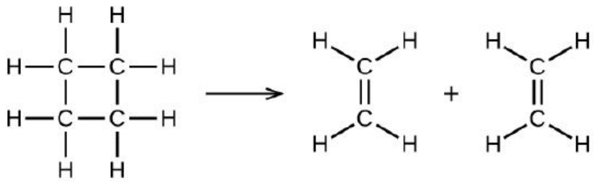
The rate equation for a unimolecular reaction is:

$$\text{rate} = k[A] \tag{3.6.4}$$

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

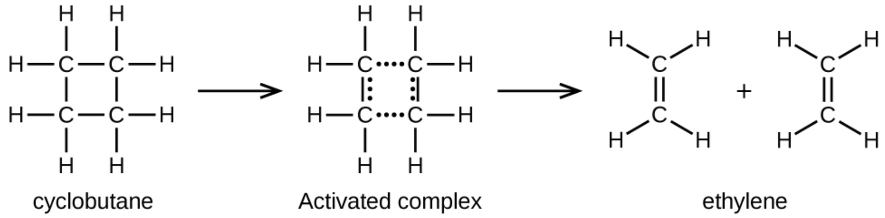
$$O_3 \longrightarrow O_2 + O \tag{3.6.5}$$

illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism. However, some unimolecular reactions may have only a single reaction in the reaction mechanism. (In other words, an elementary reaction can also be an overall reaction in some cases.) For example, the gas-phase decomposition of cyclobutane, C_4H_8, to ethylene, C_2H_4, occurs via a unimolecular, single-step mechanism:



For these unimolecular reactions to occur, all that is required is the separation of parts of single reactant molecules into products.

Chemical bonds do not simply fall apart during chemical reactions. Energy is required to break chemical bonds. The activation energy for the decomposition of C_4H_8, for example, is 261 kJ per mole. This means that it requires 261 kilojoules to distort one mole of these molecules into activated complexes that decompose into products:



In a sample of C_4H_8, a few of the rapidly moving C_4H_8 molecules collide with other rapidly moving molecules and pick up additional energy. When the C_4H_8 molecules gain enough energy, they can transform into an activated complex, and the formation of ethylene molecules can occur. In effect, a particularly energetic collision knocks a C_4H_8 molecule into the geometry of the activated complex. However, only a small fraction of gas molecules travel at sufficiently high speeds with large enough kinetic energies to accomplish this. Hence, at any given moment, only a few molecules pick up enough energy from collisions to react.

The rate of decomposition of C_4H_8 is directly proportional to its concentration. Doubling the concentration of C_4H_8 in a sample gives twice as many molecules per liter. Although the fraction of molecules with enough energy to react remains the same, the total number of such molecules is twice as great. Consequently, there is twice as much C_4H_8 per liter, and the reaction rate is twice as fast:

$$\text{rate} = -\frac{\Delta[\text{C}_4\text{H}_8]}{\Delta t} = k[\text{C}_4\text{H}_8] \tag{3.6.6}$$

A similar relationship applies to any unimolecular elementary reaction; the reaction rate is directly proportional to the concentration of the reactant, and the reaction exhibits first-order behavior. The proportionality constant is the rate constant for the particular unimolecular reaction.

3.6.2: Bimolecular Elementary Reactions

The collision and combination of two molecules or atoms to form an activated complex in an elementary reaction is called a bimolecular reaction. There are two types of bimolecular elementary reactions:

$$A + B \longrightarrow \text{products} \tag{3.6.7}$$

and

$$2A \longrightarrow \text{products} \tag{3.6.8}$$

For the first type, in which the two reactant molecules are different, the rate law is first-order in *A* and first order in *B*:

$$\text{rate} = k[A][B] \tag{3.6.9}$$

For the second type, in which two identical molecules collide and react, the rate law is second order in *A*:

$$\text{rate} = k[A][A] = k[A]^2 \tag{3.6.10}$$

Some chemical reactions have mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide:

$$\text{NO}_2(g) + \text{CO}(g) \longrightarrow \text{NO}(g) + \text{CO}_2(g) \tag{3.6.11}$$

(see Figure 3.6.1)

This figure provides an illustration of a reaction between two H I molecules using space filling models. H atoms are shown as white spheres, and I atoms are shown as purple spheres. On the left, two H I molecules are shownwith a small white sphere bonded to a much larger purple sphere. The label, “Two H I molecules,” appears below. An arrow points right to a similar structure in which the two molecules appear pushed together, so that the purple spheres of the two molecules are touching. Below appears the label, “Transition state.” Following another arrow, two white spheres are shown vertically oriented and bonded together with the label, “H subscript 2” above. The H subscript 2 molecule is followed by a plus sign and two purple spheres bonded together with the label, “I subscript 2” above. Below these structures is the label, “Hydrogen iodide molecules decompose to produce hydrogen H subscript 2 and iodine I subscript 2.”

Figure 3.6.1: The probable mechanism for the reaction between NO_2 and CO to yield NO and CO_2.

Bimolecular elementary reactions may also be involved as steps in a multistep reaction mechanism. The reaction of atomic oxygen with ozone is one example:

$$O(g) + O_3(g) \longrightarrow 2\,O_2(g) \tag{3.6.12}$$

3.6.3: Termolecular Elementary Reactions

An elementary termolecular reaction involves the simultaneous collision of three atoms, molecules, or ions. Termolecular elementary reactions are uncommon because the probability of three particles colliding simultaneously is less than one one-thousandth of the probability of two particles colliding. There are, however, a few established termolecular elementary reactions. The reaction of nitric oxide with oxygen appears to involve termolecular steps:

$$\begin{gathered} 2\,NO + O_2 \longrightarrow 2\,NO_2 \\ \text{rate} = k[NO]^2[O_2] \end{gathered} \tag{3.6.13}$$

Likewise, the reaction of nitric oxide with chlorine appears to involve termolecular steps:

$$\begin{gathered} 2\,NO + Cl_2 \longrightarrow 2\,NOCl \\ \text{rate} = k[NO]^2[Cl_2] \end{gathered} \tag{3.6.14}$$

3.6.4: Relating Reaction Mechanisms to Rate Laws

It's often the case that one step in a multistep reaction mechanism is significantly slower than the others. Because a reaction cannot proceed faster than its slowest step, this step will limit the rate at which the overall reaction occurs. The slowest step is therefore called the rate-limiting step, or **rate-determining step**, of the reaction (Figure 3.6.2).

Figure 3.6.2: A cattle chute is a nonchemical example of a rate-determining step. Cattle can only be moved from one holding pen to another as quickly as one animal can make its way through the chute. (credit: Loren Kerns)

Rate laws may be derived directly from the chemical equations for elementary reactions. This is *only true* for elementary reactions, and *not the case* for overall chemical reactions. The balanced equations most often encountered represent the overall change for some chemical system, and very often this is the result of some multistep reaction mechanism. In every case, we must determine the overall rate law from experimental data and deduce the mechanism from the rate law (and sometimes from other data). The reaction of NO_2 and CO provides an illustrative example:

$$NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g) \tag{3.6.15}$$

For temperatures above 225 °C, the rate law has been found to be:

$$\text{rate} = k[NO_2][CO] \tag{3.6.16}$$

The reaction is first order with respect to NO_2 and first-order with respect to CO. This is consistent with a single-step bimolecular mechanism and it is *possible* that this is the mechanism for this reaction at high temperatures.

At temperatures below 225 °C, the reaction is described by a rate law that is second order with respect to NO_2:

$$\text{rate} = k[NO_2]^2 \tag{3.6.17}$$

This is consistent with a mechanism that involves the following two elementary reactions, the first of which is slower and is therefore the rate-determining step:

$$\begin{gathered} NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g) \text{ (slow)} \\ NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g) \text{ (fast)} \end{gathered} \tag{3.6.18}$$

The rate-determining step gives a rate law showing second-order dependence on the NO_2 concentration, and the sum of the two equations gives the net overall reaction.

In general, when the rate-determining (slower) step is the first step in a mechanism, the rate law for the overall reaction is the same as the rate law for this step. However, when the rate-determining step is preceded by a step involving an *equilibrium* reaction, the rate law for the overall reaction may be more difficult to derive.

An elementary reaction is at equilibrium when it proceeds in both the forward and reverse directions at equal rates. Consider the dimerization of NO to N_2O_2, with k_1 used to represent the rate constant of the forward reaction and $k_{\text{-}1}$ used to represent the rate constant of the reverse reaction:

$$NO + NO \rightleftharpoons N_2O_2 \tag{3.6.19}$$

$$\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}} \tag{3.6.20}$$

$$k_1[NO]^2 = k_{-1}[N_2O_2] \tag{3.6.21}$$

If N_2O_2 was an intermediate in a mechanism, this expression could be rearranged to represent the concentration of N_2O_2 in the overall rate law expression using algebraic manipulation:

$$\left(\frac{k_1[NO]^2}{k_{-1}}\right) = [N_2O_2] \tag{3.6.22}$$

Example 3.6.1

Nitrogen monoxide, NO, reacts with hydrogen, H_2, according to the following equation:

$$2\,NO + 2\,H_2 \longrightarrow N_2 + 2\,H_2O$$

What would the rate law be if the mechanism for this reaction were:

$$\begin{gathered} 2\,NO + H_2 \longrightarrow N_2 + H_2O_2 \text{ (slow)} \\ H_2O_2 + H_2 \longrightarrow 2\,H_2O \text{ (fast)} \end{gathered}$$

Solution

In the given mechanism, the first step is the rate-determining step. The rate law for this step is first-order with respect to H_2 and second-order with respect to NO.

$$\text{rate} = k[NO]^2[H_2]$$

Because intermediates are present in very low amounts in reactions, and because we do not control these amounts, reaction intermedietes are not included as part of the overall rate law expression. Yet if they are involved in the rate-determining step, they can be included in an individual elementary reaction of a mechanism. Example 3.6.2 will illustrate how to derive overall rate laws from mechanisms involving equilibrium steps preceding the rate-determining step.

Example 3.6.2: Deriving the Overall Rate Law Expression for a Multistep Reaction

Mechanism Nitryl chloride (NO_2Cl) decomposes to nitrogen dioxide (NO_2) and chlorine gas (Cl_2) according to the following mechanism:

1. $2\,NO_2Cl(g) \rightleftharpoons ClO_2(g) + N_2O(g) + ClO(g)$ (fast, k_1 represents the rate constant for the forward reaction and k_{-1} the rate constant for the reverse reaction)
2. $N_2O(g) + ClO_2(g) \rightleftharpoons NO_2(g) + NOCl(g)$ (fast, k_2 for the forward reaction, k_{-2} for the reverse reaction)
3. $NOCl + ClO \longrightarrow NO_2 + Cl_2$ (slow, k_3 the rate constant for the forward reaction)

Determine the overall reaction, write the rate law expression for each elementary reaction, identify any intermediates, and determine the overall rate law expression.

Solution

For the overall reaction, simply sum the three steps, cancel intermediates, and combine like formulas:

$$2\,\mathrm{NO_2Cl}(g) \longrightarrow 2\,\mathrm{NO_2}(g) + \mathrm{Cl_2}(g)$$

Next, write the rate law expression for each elementary reaction. Remember that for elementary reactions that are part of a mechanism, the rate law expression can be derived directly from the stoichiometry:

$$\begin{aligned} k_1[\mathrm{NO_2Cl}]_2 &= k_{-1}[\mathrm{ClO_2}][\mathrm{N_2O}][\mathrm{ClO}] \\ k_2[\mathrm{N_2O}][\mathrm{ClO_2}] &= k_{-2}[\mathrm{NO_2}][\mathrm{NOCl}] \\ \mathrm{Rate} &= k_3[\mathrm{NOCl}][\mathrm{ClO}] \end{aligned}$$

The third step, which is the slow step, is the rate-determining step. Therefore, the overall rate law expression could be written as Rate = k_3 [NOCl][ClO]. However, both NOCl and ClO are intermediates. Algebraic expressions must be used to represent [NOCl] and [ClO] such that no intermediates remain in the overall rate law expression.

- Using elementary reaction 1, $[\mathrm{ClO}] = \dfrac{k_1[\mathrm{NO_2Cl}]^2}{k_{-1}[\mathrm{ClO_2}][\mathrm{N_2O}]}$.
- Using elementary reaction 2, $[\mathrm{NOCl}] = \dfrac{k_2[\mathrm{N_2O}][\mathrm{ClO_2}]}{k_{-2}[\mathrm{NO_2}]}$.

Now substitute these algebraic expressions into the overall rate law expression and simplify:

$$\begin{aligned} \mathrm{rate} &= k_3\left(\frac{k_2[\mathrm{N_2O}][\mathrm{ClO_2}]}{k_{-2}[\mathrm{NO_2}]}\right)\left(\frac{k_1[\mathrm{NO_2Cl}]^2}{k_{-1}[\mathrm{ClO_2}][\mathrm{N_2O}]}\right) \\ \mathrm{rate} &= \frac{k_3k_2k_1[\mathrm{NO_2Cl}]^2}{k_{-2}k_{-1}[\mathrm{NO_2}]} \end{aligned}$$

Notice that this rate law shows an *inverse* dependence on the concentration of one of the product species, consistent with the presence of an equilibrium step in the reaction mechanism.

Exercise 3.6.1

Atomic chlorine in the atmosphere reacts with ozone in the following pair of elementary reactions:

$$\begin{aligned} \mathrm{Cl} + \mathrm{O_3}(g) &\longrightarrow \mathrm{ClO}(g) + \mathrm{O_2}(g) \quad (\text{rate constant } k_1) \\ \mathrm{ClO}(g) + \mathrm{O} &\longrightarrow \mathrm{Cl}(g) + \mathrm{O_2}(g) \quad (\text{rate constant } k_2) \end{aligned}$$

The second step is the rate-determining step. Determine the overall reaction, write the rate law expression for each elementary reaction, identify any intermediates, and determine the overall rate law expression.

Answer

- overall reaction: $\mathrm{O_3}(g) + \mathrm{O} \longrightarrow 2\,\mathrm{O_2}(g)$
- $\mathrm{rate}_1 = k_1[\mathrm{O_3}][\mathrm{Cl}]$; $\mathrm{rate}_2 = k_2[\mathrm{ClO}][\mathrm{O}]$
- intermediate: ClO(g)
- overall rate = $k_2k_1[\mathrm{O_3}][\mathrm{Cl}][\mathrm{O}]$

Summary

The sequence of individual steps, or elementary reactions, by which reactants are converted into products during the course of a reaction is called the reaction mechanism. The overall rate of a reaction is determined by the rate of the slowest step, called the rate-determining step. Unimolecular elementary reactions have first-order rate laws, while bimolecular elementary reactions have second-order rate laws. By comparing the rate laws derived from a reaction mechanism to that determined experimentally, the mechanism may be deemed either incorrect or plausible.

3.6.4.1: Footnotes

1. This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

3.6.4.2: Glossary

bimolecular reaction

elementary reaction involving the collision and combination of two reactant species

elementary reaction

reaction that takes place precisely as depicted in its chemical equation

intermediate

molecule or ion produced in one step of a reaction mechanism and consumed in another

molecularity

number of reactant species (atoms, molecules or ions) involved in an elementary reaction

rate-determining step

(also, rate-limiting step) slowest elementary reaction in a reaction mechanism; determines the rate of the overall reaction

reaction mechanism

stepwise sequence of elementary reactions by which a chemical change takes place

termolecular reaction

elementary reaction involving the simultaneous collision and combination of three reactant species

unimolecular reaction

elementary reaction involving the rearrangement of a single reactant species to produce one or more molecules of product

Contributors and Attributions

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3.7: Catalysis

Learning Objectives

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

We have seen that the rate of many reactions can be accelerated by catalysts. A catalyst speeds up the rate of a reaction by lowering the activation energy; in addition, the catalyst is regenerated in the process. Several reactions that are thermodynamically favorable in the absence of a catalyst only occur at a reasonable rate when a catalyst is present. One such reaction is catalytic hydrogenation, the process by which hydrogen is added across an alkene C=C bond to afford the saturated alkane product. A comparison of the reaction coordinate diagrams (also known as energy diagrams) for catalyzed and uncatalyzed alkene hydrogenation is shown in Figure $3.7.1$.

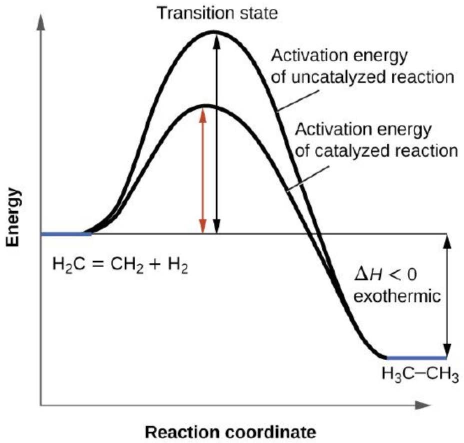


Figure $3.7.1$: This graph compares the reaction coordinates for catalyzed and uncatalyzed alkene hydrogenation.

A graph is shown with the label, “Reaction coordinate,” on the x-axis and the label,“Energy,” on the y-axis. Approximately halfway up the y-axis, a short portion of a black concave down curve which has a horizontal line extended from it across the graph. The left end of this line is labeled “H subscript 2 C equals C H subscript 2 plus H subscript 2.” The black concave down curve extends upward to reach a maximum near the height of the y-axis. The peak of this curve is labeled, “Transition state.” A double sided arrow extends from the horizontal line to the peak of the curve. This arrow is labeled, “Activation energy of Uncatalyzed reation.” From the peak, the curve continues downward to a second horizontally flattened region well below the origin of the curve near the x-axis. This flattened region is shaded in blue and is labeled “H subscript 3 C dash C H subscript 3.” A double sided arrow is drawn from the lowers part of this curve at the far right of the graph to the line extending across the graph above it. This arrow is labeled, “capital delta H less than 0 : exothermic.” A second curve is drawn with the same flattened regions at the start and end of the curve. The height of this curve is about two-thirds the height of the first curve. A double sided arrow is drawn from the horizontal line that originates at the left side of the graph to the peak of this second curve. This arrow is labeled, “Activation energy of catalyzed reaction.”

Catalysts function by providing an alternate reaction mechanism that has a lower activation energy than would be found in the absence of the catalyst. In some cases, the catalyzed mechanism may include additional steps, as depicted in the reaction diagrams shown in Figure $3.7.2$ This lower activation energy results in an increase in rate as described by the Arrhenius equation. Note that a catalyst decreases the activation energy for both the forward and the reverse reactions and hence *accelerates both the forward and the reverse reactions*. Consequently, the presence of a catalyst will permit a system to reach equilibrium more quickly, but it has no effect on the position of the equilibrium as reflected in the value of its equilibrium constant (see the later chapter on chemical equilibrium).

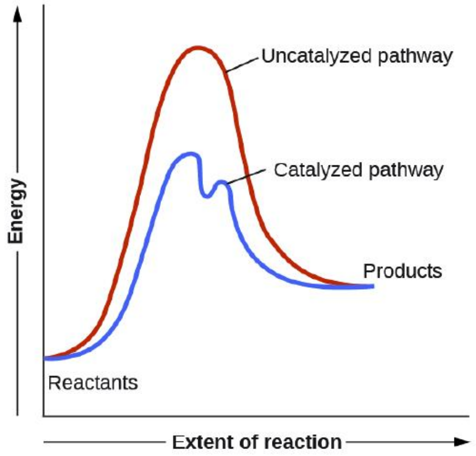
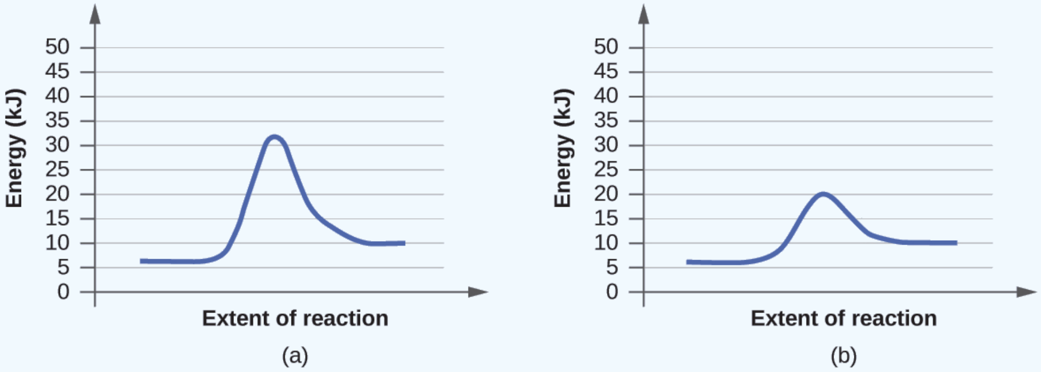


Figure $3.7.2$: This potential energy diagram shows the effect of a catalyst on the activation energy. The catalyst provides a different reaction path with a lower activation energy. As shown, the catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

A graph is shown with the label, “Extent of reaction,” appearing in a right pointing arrow below the x-axis and the label, “Energy,” in an upward pointing arrow just left of the y-axis. Approximately one-fifth of the way up the y-axis, a very short, somewhat flattened portion of both a red and a blue curve are shown. This region is labeled “Reactants.” A red concave down curve extends upward to reach a maximum near the height of the y-axis. This curve is labeled, “Uncatalyzed pathway.” From the peak, the curve continues downward to a second horizontally flattened region at a height of about one-third the height of the y-axis. This flattened region is labeled, “Products.” A second curve is drawn in blue with the same flattened regions at the start and end of the curve. The height of this curve is about two-thirds the height of the first curve and just right of its maximum, the curve dips low, then rises back and continues a downward trend at a lower height, but similar to that of the red curve. This blue curve is labeled, “Catalyzed pathway.”

✓ Example 3.7.1: Using Reaction Diagrams to Compare Catalyzed Reactions

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Identify which diagram suggests the presence of a catalyst, and determine the activation energy for the catalyzed reaction:



In this figure, two graphs are shown. The x-axes are labeled, “Extent of reaction,” and the y-axes are labeled, “Energy (k J).” The y-axes are marked off from 0 to 50 in intervals of five. In a, a blue curve is shown. It begins with a horizontal segment at about 6. The curve then rises sharply near the middle to reach a maximum of about 32 and similarly falls to another horizontal segment at about 10. In b, the curve begins and ends similarly, but the maximum reached near the center of the graph is only 20.

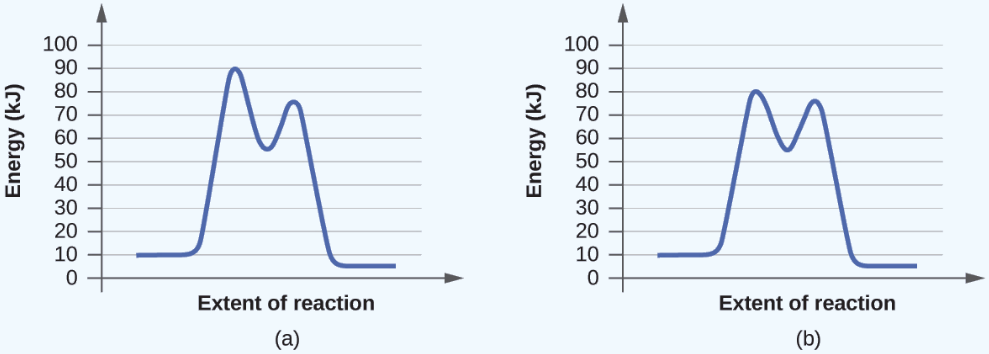
Solution

A catalyst does not affect the energy of reactant or product, so those aspects of the diagrams can be ignored; they are, as we would expect, identical in that respect. There is, however, a noticeable difference in the transition state, which is distinctly lower in diagram (b) than it is in (a). This indicates the use of a catalyst in diagram (b). The activation energy is the difference between the energy of the starting reagents and the transition state—a maximum on the reaction coordinate diagram. The reagents are at 6 kJ and the transition state is at 20 kJ, so the activation energy can be calculated as follows:

$$E_a = 20\text{ kJ} - 6\text{ kJ} = 14\text{ kJ} \tag{3.7.1}$$

Exercise 3.7.1

Determine which of the two diagrams here (both for the same reaction) involves a catalyst, and identify the activation energy for the catalyzed reaction:



In this figure, two graphs are shown. The x-axes are labeled, "Extent of reaction," and the y-axes are labeledc "Energy (k J)." The y-axes are marked off from 0 to 100 at intervals of 10. In a, a blue curve is shown. It begins with a horizontal segment at about 10. The curve then rises sharply near the middle to reach a maximum of about 91, then sharply falls to about 52, again rises sharply to about 73 and falls to another horizontal segment at about 5. In b, the curve begins and ends similarly, but the first peak reaches about 81, drops to about 55, then rises to about 77 before falling to the horizontal region at about 5.

Answer

Diagram (b) is a catalyzed reaction with an activation energy of about 70 kJ.

3.7.1: Homogeneous Catalysts

A homogeneous catalyst is present in the same phase as the reactants. It interacts with a reactant to form an intermediate substance, which then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form product. As an important illustration of homogeneous catalysis, consider the earth's ozone layer. Ozone in the upper atmosphere, which protects the earth from ultraviolet radiation, is formed when oxygen molecules absorb ultraviolet light and undergo the reaction:

$$3\,O_2(g) \xrightarrow{hv} 2\,O_3(g) \tag{3.7.2}$$

Ozone is a relatively unstable molecule that decomposes to yield diatomic oxygen by the reverse of this equation. This decomposition reaction is consistent with the following mechanism:

$$\begin{aligned} O_3 &\longrightarrow O_2 + O \\ O + O_3 &\longrightarrow 2\,O_2 \end{aligned} \tag{3.7.3}$$

The presence of nitric oxide, NO, influences the rate of decomposition of ozone. Nitric oxide acts as a catalyst in the following mechanism:

$$\begin{gathered} NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g) \\ O_3(g) \longrightarrow O_2(g) + O(g) \\ NO_2(g) + O(g) \longrightarrow NO(g) + O_2(g) \end{gathered} \tag{3.7.4}$$

The overall chemical change for the catalyzed mechanism is the same as:

$$2\,O_3(g) \longrightarrow 3\,O_2(g) \tag{3.7.5}$$

The nitric oxide reacts and is regenerated in these reactions. It is not permanently used up; thus, it acts as a catalyst. The rate of decomposition of ozone is greater in the presence of nitric oxide because of the catalytic activity of NO. Certain compounds that contain chlorine also catalyze the decomposition of ozone.

Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina (Figure 3.7.3), and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone." Molina, a Mexican citizen, carried out the majority of his work at the Massachusetts Institute of Technology (MIT).

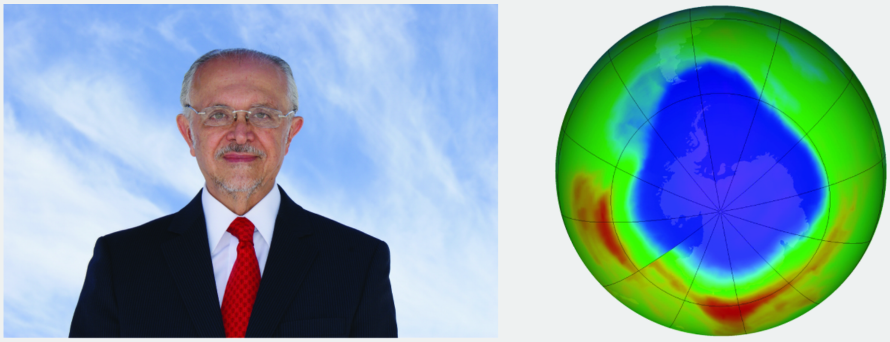

(a) (b)

Figure 3.7.3: (a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his research on (b) the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

A photograph is shown of Mario Molina. To the right of the photo, an image of Earth's southern hemisphere is shown with a central circular region in purple with a radius of about half that of the entire hemisphere. Just outside this region is a narrow royal blue band, followed by an outer thin turquoise blue band. The majority of the outermost region is green. Two small bands of yellow are present in the lower regions of the image.

In 1974, Molina and Rowland published a paper in the journal *Nature* (one of the major peer-reviewed publications in the field of science) detailing the threat of chlorofluorocarbon gases to the stability of the ozone layer in earth's upper atmosphere. The ozone layer protects earth from solar radiation by absorbing ultraviolet light. As chemical reactions deplete the amount of ozone in the upper atmosphere, a measurable "hole" forms above Antarctica, and an increase in the amount of solar ultraviolet radiation— strongly linked to the prevalence of skin cancers—reaches earth's surface. The work of Molina and Rowland was instrumental in the adoption of the Montreal Protocol, an international treaty signed in 1987 that successfully began phasing out production of chemicals linked to ozone destruction.

Molina and Rowland demonstrated that chlorine atoms from human-made chemicals can catalyze ozone destruction in a process similar to that by which NO accelerates the depletion of ozone. Chlorine atoms are generated when chlorocarbons or chlorofluorocarbons—once widely used as refrigerants and propellants—are photochemically decomposed by ultraviolet light or react with hydroxyl radicals. A sample mechanism is shown here using methyl chloride:

\[\ce{CH3Cl + OH ⟶ Cl + other\: products} \nonumber \]

Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:

$$\mathrm{Cl} + \mathrm{O_3} \longrightarrow \mathrm{ClO} + \mathrm{O_2}$$
$$\mathrm{ClO} + \mathrm{O} \longrightarrow \mathrm{Cl} + \mathrm{O_2}$$
$$\text{overall Reaction: } \mathrm{O_3} + \mathrm{O} \longrightarrow 2\,\mathrm{O_2}$$

A single monatomic chlorine can break down thousands of ozone molecules. Luckily, the majority of atmospheric chlorine exists as the catalytically inactive forms Cl_2 and $ClONO_2$.

3.7.2: Glucose-6-Phosphate Dehydrogenase Deficiency

Enzymes in the human body act as catalysts for important chemical reactions in cellular metabolism. As such, a deficiency of a particular enzyme can translate to a life-threatening disease. G6PD (glucose-6-phosphate dehydrogenase) deficiency, a genetic condition that results in a shortage of the enzyme glucose-6-phosphate dehydrogenase, is the most common enzyme deficiency in humans. This enzyme, shown in Figure 3.7.4, is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells (FIgure 3.7.5).

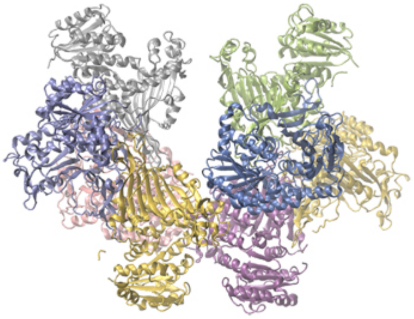


Figure $3.7.4$: Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

A colorful model of the Glucose-6-phosphate dehydrogenase structure is shown. The molecule has two distinct lobes which are filled with spiraled ribbon-like regions of yellow, lavender, blue, silver, green, and pink.

A disruption in this pathway can lead to reduced glutathione in red blood cells; once all glutathione is consumed, enzymes and other proteins such as hemoglobin are susceptible to damage. For example, hemoglobin can be metabolized to bilirubin, which leads to jaundice, a condition that can become severe. People who suffer from G6PD deficiency must avoid certain foods and medicines containing chemicals that can trigger damage their glutathione-deficient red blood cells.

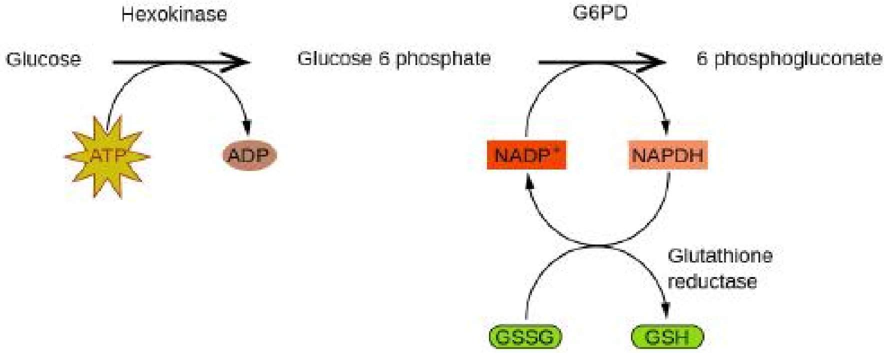


Figure $3.7.5$: In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NAPDH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

A reaction mechanism is diagrammed in this figure. At the left, the name Glucose is followed by a horizontal, right pointing arrow, labeled, "Hexokinase." Below this arrow and to the left is a yellow star shape labeled, "A T P." A curved arrow extends from this shape to the right pointing arrow, and down to the right to a small brown oval labeled, "A D P." To the right of the horizontal arrow is the name Glucose 6 phosphate, which is followed by another horizontal, right pointing arrow which is labeled, "G 6 P D." A small orange rectangle below and left of this arrow is labeled "N A D P superscript plus." A curved arrow extends from this shape to the right pointing arrow, and down to the right to a small salmon-colored rectangle labeled "N A P D H." A curved arrow extends from this shape below and to the left, back to the orange rectangle labeled, "N A D P superscript plus." Another curved arrow extends from a green oval labeled "G S S G" below the orange rectangle, up to the arrow curving back to the orange rectangle. This last curved arrow continues on to the lower right to a second green oval labeled, "G S H." The end of this curved arrow is labeled, "Glutathione reductase." To the right of the rightmost horizontal arrow appears the name 6 phosphogluconate.

3.7.3: Heterogeneous Catalysts

A heterogeneous catalyst is a catalyst that is present in a different phase (usually a solid) than the reactants. Such catalysts generally function by furnishing an active surface upon which a reaction can occur. Gas and liquid phase reactions catalyzed by heterogeneous catalysts occur on the surface of the catalyst rather than within the gas or liquid phase.

Heterogeneous catalysis has at least four steps:

1. Adsorption of the reactant onto the surface of the catalyst
2. Activation of the adsorbed reactant
3. Reaction of the adsorbed reactant
4. Diffusion of the product from the surface into the gas or liquid phase (desorption).

Any one of these steps may be slow and thus may serve as the rate determining step. In general, however, in the presence of the catalyst, the overall rate of the reaction is faster than it would be if the reactants were in the gas or liquid phase.

Figure 3.7.6 illustrates the steps that chemists believe to occur in the reaction of compounds containing a carbon–carbon double bond with hydrogen on a nickel catalyst. Nickel is the catalyst used in the hydrogenation of polyunsaturated fats and oils (which contain several carbon–carbon double bonds) to produce saturated fats and oils (which contain only carbon–carbon single bonds).

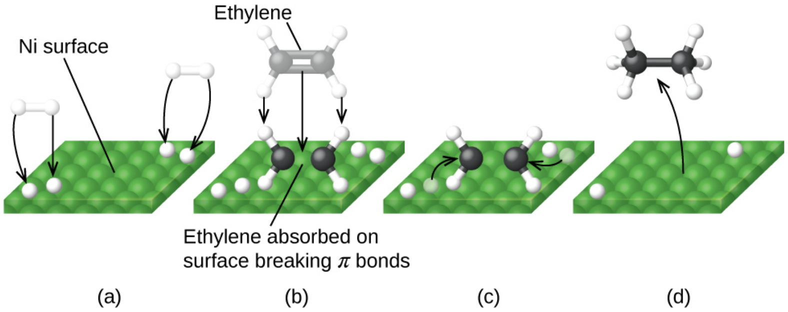


Figure 3.7.6: There are four steps in the catalysis of the reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$ *by nickel. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the π-bond and forming Ni–C bonds. (c) Atoms diffuse across the surface and form new C–H bonds when they collide. (d)* C_2H_6 *molecules escape from the nickel surface, since they are not strongly attracted to nickel.*

In this figure, four diagrams labeled a through d are shown. In each, a green square surface is shown in perspective to provide a three-dimensional appearance. In a, the label “N i surface” is placed above with a line segment extending to the green square. At the lower left and upper right, pairs of white spheres bonded tougher together appear as well as white spheres on the green surface. Black arrows are drawn from each of the white spheres above the surface to the white sphere on the green surface. In b, the white spheres are still present on the green surface. Near the center of this surface is a molecule with two central black spheres with a double bond indicated by two horizontal black rods between them. Above and below to the left and right, a total of four white spheres are connected to the black spheres with white rods. A line segment extends from this structure to the label, “Ethylene absorbed on surface breaking pi bonds.” Just above this is a nearly identical structure greyed out with three downward pointing arrows to the black and white structure to indicate downward motion. The label “Ethylene” at the top of the diagram is connected to the greyed out structure with a line segment. In c, the diagram is very similar to b except that the greyed out structure and labels are gone and one of the white spheres near the black and white structure in each pair on the green surface is greyed out. Arrows point from the greyed out white spheres to the double bond between the two black spheres. In d, only a single white sphere remains from each pair in the green surface. A curved arrow points from the middle of the green surface to a model above with two central black spheres with a single black rod indicating a single bond between them. Each of the black rods has three small white spheres bonded as indicated by white rods between the black spheres and the small white spheres. The four bonds around each black sphere are evenly distributed about the black spheres.

Other significant industrial processes that involve the use of heterogeneous catalysts include the preparation of sulfuric acid, the preparation of ammonia, the oxidation of ammonia to nitric acid, and the synthesis of methanol, CH_3OH. Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles (Figure 3.7.7).

Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. Catalytic converters take advantage of all five factors that affect the speed of chemical reactions to ensure that exhaust emissions are as safe as possible.

By utilizing a carefully selected blend of catalytically active metals, it is possible to effect complete combustion of all carbon-containing compounds to carbon dioxide while also reducing the output of nitrogen oxides. This is particularly impressive when we consider that one step involves adding more oxygen to the molecule and the other involves removing the oxygen (Figure 3.7.6).

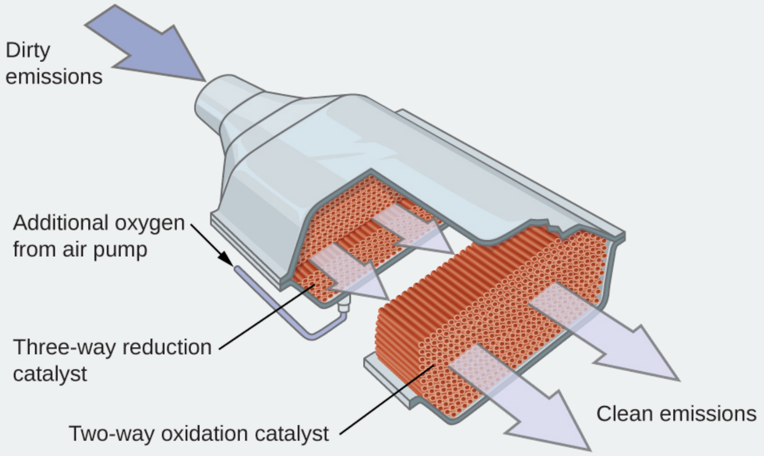


Figure 3.7.6: A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

An image is shown of a catalytic converter. At the upper left, a blue arrow pointing into a pipe that enters a larger, widened chamber is labeled, “Dirty emissions.” A small black arrow that points to the lower right is positioned along the upper left side of the widened region. This arrow is labeled, “Additional oxygen from air pump.” The image shows the converter with the upper surface removed, exposing a red-brown interior. The portion of the converter closest to the dirty emissions inlet shows small, round components in an interior layer. This layer is labeled “Three-way reduction catalyst.” The middle region shows closely packed small brown rods that are aligned parallel to the dirty emissions inlet pipe. The final quarter of the interior of the catalytic converter again shows a layer of closely packed small red brown circles. Two large light grey arrows extend from this layer to the open region at the lower right of the image to the label “Clean emissions.”

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion nitric oxide into dinitrogen and oxygen as well as the conversion of carbon monoxide and hydrocarbons such as octane into carbon dioxide and water vapor:

$$2\,NO_2(g) \longrightarrow N_2(g) + 2\,O_2(g)$$
$$[5pt]2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$$
$$[5pt]2\,C_8H_{18}(g) + 25\,O_2(g) \longrightarrow 16\,CO_2(g) + 18\,H_2O(g)$$

In order to be as efficient as possible, most catalytic converters are preheated by an electric heater. This ensures that the metals in the catalyst are fully active even before the automobile exhaust is hot enough to maintain appropriate reaction temperatures.

3.7.4: Enzyme Structure and Function

The study of enzymes is an important interconnection between biology and chemistry. Enzymes are usually proteins (polypeptides) that help to control the rate of chemical reactions between biologically important compounds, particularly those that are involved in cellular metabolism. Different classes of enzymes perform a variety of functions, as shown in Table 3.7.1.

ATP hydrolysis.”" data-quail-id="131" data-mt-width="1016">

Table 3.7.1: Classes of Enzymes and Their Functions

Class	Function
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Enzyme molecules possess an active site, a part of the molecule with a shape that allows it to bond to a specific substrate (a reactant molecule), forming an enzyme-substrate complex as a reaction intermediate. There are two models that attempt to explain how this active site works. The most simplistic model is referred to as the lock-and-key hypothesis, which suggests that the molecular shapes of the active site and substrate are complementary, fitting together like a key in a lock. The induced fit hypothesis, on the other hand, suggests that the enzyme molecule is flexible and changes shape to accommodate a bond with the substrate. This is not to suggest that an enzyme's active site is completely malleable, however. Both the lock-and-key model and the induced fit model account for the fact that enzymes can only bind with specific substrates, since in general a particular enzyme only catalyzes a particular reaction (Figure $3.7.7$).

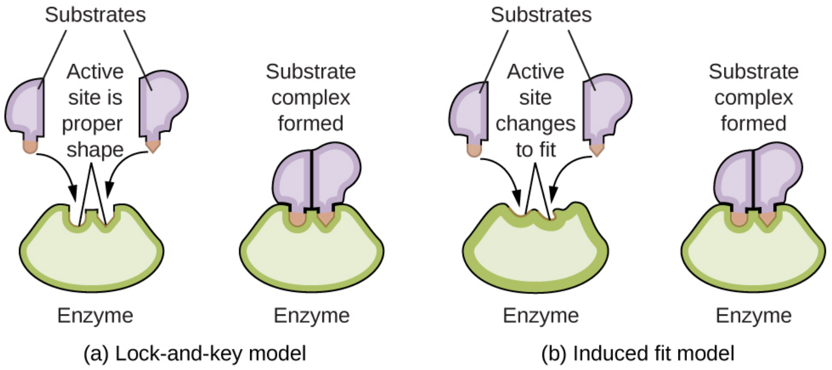


Figure $3.7.7$: (a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

A diagram is shown of two possible interactions of an enzyme and a substrate. In a, which is labeled "Lock-and-key," two diagrams are shown. The first shows a green wedge-like shape with two small depressions in the upper surface of similar size, but the depression on the left has a curved shape, and the depression on the right has a pointed shape. This green shape is labeled "Enzyme." Just above this shape are two smaller, irregular, lavender shapes each with a projection from its lower surface. The lavender shape on the left has a curved projection which matches the shape of the depression on the left in the green shape below. This projection is shaded orange and has a curved arrow extending from in to the matching depression in the green shape below. Similarly, the lavender shape on the right has a projection with a pointed tip which matches the shape of the depression on the right in the green shape below. This projection is shaded orange and has a curved arrow extending from in to the matching depression in the green shape below. Two line segments extend from the depressions in the green shape to form an inverted V shape above the depressions. Above this and between the lavender shapes is the label, "Active site is proper shape." The label "Substrates" is at the very top of the diagram with line segments extending to the two lavender shapes. To the right of this diagram is a second diagram showing the lavender shapes positioned next to each other, fit snugly into the depressions in the green shape, which is labeled "Enzyme." Above this diagram is the label, "Substrate complex formed." In b, which is labeled "Induced fit," two diagrams are shown. The first shows a green wedge-like shape with two small depressions in the upper surface of similar size, but irregular shape. This green shape is labeled "Enzyme." Just above this shape are two smaller irregular lavender shapes each with a projection from its lower surface. The lavender shape on the left has a curved projection. This projection is shaded orange and has a curved arrow extending from it to the irregular depression just below it in the green shape below. Similarly, the lavender shape on the right has a projection with a pointed tip. This projection is shaded orange and has a curved arrow extending from it to the irregular depression just below it in the green shape below. Two line segments extend from the depressions in the green shape to form an inverted V shape above the depressions. Above this and between the lavender shapes is the label, "Active site changes to fit." The label, "Substrates" is at the very top of the diagram with line segments extending to the two lavender shapes. To the right of this diagram is a second diagram showing the purple shapes positioned next to each other, fit snugly into the depressions in the green shape, which is labeled "Enzyme." Above this diagram is the label "Substrate complex formed." The projections from the lavender shapes match the depression shapes in the green shape, resulting in a proper fit.

Summary

Catalysts affect the rate of a chemical reaction by altering its mechanism to provide a lower activation energy. Catalysts can be homogenous (in the same phase as the reactants) or heterogeneous (a different phase than the reactants).

Footnotes

1. "The Nobel Prize in Chemistry 1995," Nobel Prize.org, accessed February 18, 2015, Nobel Prizes Chemistry [www.nobelprize.org].

Glossary

heterogeneous catalyst

catalyst present in a different phase from the reactants, furnishing a surface at which a reaction can occur

homogeneous catalyst

catalyst present in the same phase as the reactants

3.E: Kinetics (Exercises)

3.E.1: 12.1: Chemical Reaction Rates

3.E.1.1: Q12.1.1

What is the difference between average rate, initial rate, and instantaneous rate?

Solution

First, a general reaction rate must be defined to know what any variation of a rate is. The reaction rate is defined as the measure of the change in concentration of the reactants or products per unit time. The rate of a chemical reaction is not a constant and rather changes continuously, and can be influenced by temperature. Rate of a reaction can be defined as the disappearance of any reactant or appearance of any product. Thus, an average rate is the average reaction rate over a given period of time in the reaction, the instantaneous rate is the reaction rate at a specific given moment during the reaction, and the initial rate is the instantaneous rate at the very start of the reaction (when the product begins to form).

The instantaneous rate of a reaction can be denoted as

$$\lim_{\Delta t \to 0} \frac{\Delta[concentration]}{\Delta t}$$

3.E.1.2: Q12.1.2

Ozone decomposes to oxygen according to the equation $2\,O_3(g) \longrightarrow 3\,O_2(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.

Solution

For the general reaction, aA ---> bB, the rate of the reaction can be expressed in terms of the disappearance of A or the appearance of B over a certain time period as follows.

$$-\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t} \tag{3.E.1}$$

We want the rate of a reaction to be positive, but the change in the concentration of a reactant, A, will be negative because it is being used up to be transformed into product, B. Therefore, when expressing the rate of the reaction in terms of the change in the concentration of A, it is important to add a negative sign in front to ensure the overall rate positive.

Lastly, the rate must be normalized according to the stoichiometry of the reaction. In the decomposition of ozone to oxygen, two moles of ozone form three moles of oxygen gas. This means that the increase in oxygen gas will be 1.5 times as great as the decrease in ozone. Because the rate of the reaction should be able to describe both species, we divide the change in concentration by its stoichiometric coefficient in the balanced reaction equation to deal with this issue.

Therefore, the rate of the reaction of the decomposition of ozone into oxygen gas can be described as follows:

$$Rate = -\frac{\Delta[O3]}{2\Delta T} = \frac{\Delta[O2]}{3\Delta T} \tag{3.E.2}$$

Answer

$$Rate=-\frac{Δ[O3]}{2ΔT}=\frac{Δ[O2]}{3ΔT}\]

3.E.1.3: Q12.1.3

In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction $Cl_2(g) + 3\,F_2(g) \longrightarrow 2\,ClF_3(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of Cl_2 and F_2 and the formation of ClF_3.

Solution

In this problem we are asked to write the equation that relates rate expressions in terms of disappearance of the reactants of the equation and in terms of the formation of the product. A reaction rate gives insight to how rate is affected as a function of concentration of the substances in the equation. Rates can often be expressed on graphs of concentration vs time expressed in change (Δ) of concentration and time and in a short enough time interval, the instantaneous rate can be approximated. If we were to analyze the reaction given, the graph would demonstrate that Cl_2 decreases, that F_2 decreases 3 times as quickly, and then ClF_3 increases at a rate doubles. The reactants are being used and converted to product so they decrease while products increase.

For this problem, we can apply the general formula of a rate to the specific aspects of a problem where the general form follows:

$$aA + bB \longrightarrow cC + dD$$

.

And the rate can then be written as $rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$. Here the negative signs are used to keep the convention of expressing rates as positive numbers.

In this specific case we use the stoichiometry to get the specific rates of disappearance and formation (back to what was said in the first paragraph). So, the problem just involves referring the to the equation and its balanced coefficients. Based upon the equation we see that Cl_2 is a reactant and has no coefficient, F_2 has a coefficient of 3 and is also used up, and then ClF_3 is a product that increases two-fold with a coefficient of 2. So, the rate here can be written as:

$$rate = -\frac{\Delta[Cl_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[F_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[ClF_3]}{\Delta t}$$

Answer

$$\text{rate} = +\frac{1}{2}\frac{\Delta[\text{ClF}_3]}{\Delta t} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[\text{F}_2]}{\Delta t}$$

3.E.1.4: Q12.1.4

A study of the rate of dimerization of C_4H_6 gave the data shown in the table:

$$2\,\text{C}_4\text{H}_6 \longrightarrow \text{C}_8\text{H}_{12}$$

Time (s)	0	1600	3200	4800	6200
[C_4H_6] (*M*)	1.00×10^{-2}	5.04×10^{-3}	3.37×10^{-3}	2.53×10^{-3}	2.08×10^{-3}

a. Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.
b. Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus [C_4H_6]. What are the units of this rate?
c. Determine the average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s from the rates found in parts (a) and (b).

Solution

1.) The average rate of dimerization is the change in concentration of a reactant per unit time. In this case it would be:

$$rate\ of\ dimerization = -\frac{\Delta[C_4H_6]}{\Delta t}$$

Rate of dimerization between 0 s and 1600 s:

$$rate\ of\ dimerization = -\frac{5.04\times10^{-3}M - 1.00\times10^{-2}M}{1600s - 0s}$$

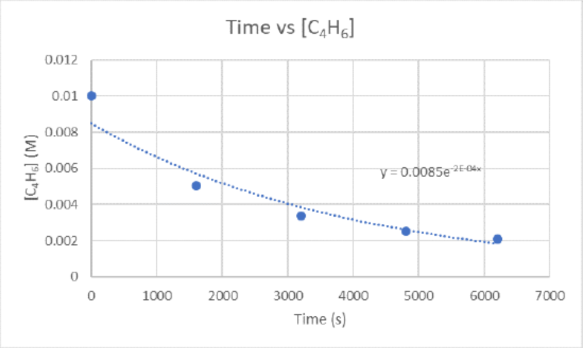
$$rate\ of\ dimerization = 3.10\times10^{-6}\,\frac{M}{s}$$

Rate of dimerization between 1600 s and 3200 s:

$$rate\ of\ dimerization = -\frac{3.37\times10^{-3}M - 5.04\times10^{-3}M}{3200s - 1600s}$$

$$rate\ of\ dimerization = 1.04\times10^{-6}\,\frac{M}{s}$$

2.) The instantaneous rate of dimerization at 3200 s can be found by graphing time versus [C_4H_6].



Because you want to find the rate of dimerization at 3200 s, you need to find the slope between 1600 s and 3200 s and also 3200 s and 4800 s.

For the slope between 1600 s and 3200 s use the points (1600 s, 5.04 x 10^{-3} M) and (3200 s, 3.37 x 10^{-3} M)

$$\frac{3.37\times10^{-3}M{-}5.04\times10^{-3}M}{3200s{-}1600s}$$

$$\frac{-0.00167M}{1600s}$$

$$-1.04\times10^{-6}\,\frac{M}{s}$$

For the slope between 3200 s and 4800 s use the points (3200s, 3.37 x 10^{-3} M) and (4800s, 2.53 x 10^{-3} M)

$$\frac{2.53\times10^{-3}M{-}3.37\times10^{-3}M}{4800s{-}3200s}$$

$$\frac{-8.4\times10^{-4}M}{1600s}$$

$$-5.25\times10^{-7}\,\frac{M}{s}$$

Take the two slopes you just found and find the average of them to get the instantaneous rate of dimerization.

$$\frac{-1.04\times10^{-6}\frac{M}{s}+-5.25\times x10^{-7}\frac{M}{s}}{2}$$

$$\frac{-1.565\times10^{-6}\frac{M}{s}}{2}$$

$$-7.83\times10^{-}7\frac{M}{s}$$

The instantaneous rate of dimerization is $-7.83\times10^{-}7\frac{M}{s}$ and the units of this rate is $\frac{M}{s}$.

3.) The average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s can be found by using our answers from part a and b. If you look back up at the original equation, you could see that C_4H_6 and C_8H_{12} are related in a two to one ratio. For every two moles of C_4H_6 used, there is one mole of C_8H_{12} produced.

For this reaction, the average rate of dimerization and the average rate of formation can be linked through this equation:

$$\frac{-1}{2}\frac{\Delta[C_4H_6]}{\Delta t}=\frac{\Delta[C_8H_{12}]}{\Delta t}$$

Notice that reactant side is negative because the reactants are being used up in the reaction.

So, for the average rate of formation of C_8H_{12} at 1600 s, use the rate of dimerization between 0 s and 1600 s we found earlier and plug into the equation:

$$\frac{-1}{2}\times3.10\times10^{-6}\,\frac{M}{s}=\frac{\Delta[C_8H_{12}]}{\Delta t}$$

$$\frac{\Delta[C_8H_{12}]}{\Delta t}=1.55\times10^{-6}\,\frac{M}{s}$$

The average rate of formation for C_8H_{12} at 1600 s is $1.55\times10^{-6}\,\frac{M}{s}$. The rate of formation will be positive because products are being formed.

The instantaneous rate of formation for C_8H_{12} can be linked to the instantaneous rate of dimerization by this equation:

$$\frac{-1}{2}\frac{d[C_4H_6]}{dt} = \frac{d[C_8H_{12}]}{dt}$$

So, for the instantaneous rate of formation for C_8H_{12} at 3200 s, use the value of instantaneous rate of dimerization at 3200 s found earlier and plug into the equation:

$$\frac{-1}{2} \times -7.83 \times 10^{-}7\frac{M}{s} = \frac{d[C_8H_{12}]}{dt}$$

$$\frac{d[C_8H_{12}]}{dt} = -3.92 \times 10^{-7}\frac{M}{s}$$

The instantaneous rate of formation for C_8H_{12} at 3200 s is $-3.92 \times 10^{-}7\frac{M}{s}$

Answer

a. $3.10 \times 10^{-6}\frac{M}{s}$ and $1.04 \times 10^{-6}\frac{M}{s}$
b. $-7.83 \times 10^{-}7\frac{M}{s}$ and $\frac{M}{s}$
c. $-3.92 \times 10^{-}7\frac{M}{s}$

3.E.1.5: Q12.1.5

A study of the rate of the reaction represented as $2A \longrightarrow B$ gave the following data:

Time (s)	0.0	5.0	10.0	15.0	20.0	25.0	35.0
[A] (M)	1.00	0.952	0.625	0.465	0.370	0.308	0.230

a. Determine the average rate of disappearance of A between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.
b. Estimate the instantaneous rate of disappearance of A at 15.0 s from a graph of time versus $[A]$. What are the units of this rate?
c. Use the rates found in parts (a) and (b) to determine the average rate of formation of B between 0.00 s and 10.0 s, and the instantaneous rate of formation of B at 15.0 s.

Solution

Equations: $\frac{-\triangle A}{\triangle time}$ and Rate=$\frac{-\triangle A}{2\triangle time} = \frac{\triangle B}{time}$

Solve: 1.)The change in A from 0s to 10s is .625-1=-.375 so $\frac{-\triangle A}{\triangle time}$ =.375/10= **0.0374 M/s**

Similarly, the change in A from 10 to 20 seconds is .370-.625=-.255 so $\frac{-\triangle A}{\triangle time}$ =.255/20-10= **0.0255M/s**

2.) We can estimate the rate law graphing the points against different order equations to determine the right order.

Zero Order:

$$\frac{d[A]}{dt} = -k$$

$$\int_{A_\circ}^{A} d[A] = -k\int_0^t dt$$

$$[A] = -kt + [A_\circ]$$

First Order:

$$\frac{d[A]}{dt} = -k[A]$$

$$\int_{A_\circ}^{A} \frac{d[A]}{[A]} = -kdt$$

$$Ln(A) = -kt + Ln(A_\circ)$$

Second Order:

$$\frac{d[A]}{dt} = -k[A]^2$$

$$\int_{A\circ}^{A} \frac{d[A]}{[A]^2} = -k\int_0^t dt$$

$$\frac{1}{[A]} = kt + \frac{1}{[A_\circ]}$$

Now that we have found the linear from of each order we will plot the points vs an [A] y-axis, a Ln(A) y-axis, and a 1/[A] y-axis. whichever of the plots has the most linear points will give us a good idea of the order and the slope will be the k value.

Here we notice that the second order is most linear so we conclude the Rate to be..

$$\frac{-d[A]}{2dt} = k[A]^2$$

At 15 seconds [A]=.465 and from the slope of the graph we find k=.116.so if we plug this data in and multiply both sides by 2 to get rid of the 2 in the denominator on the left side of the equation we find that the rate of disappearance of A is .05 M/s where the units are equivalent to [mol*L^{-1}*s^{-1}]

3.) Using the equation $\frac{-\triangle A}{2\triangle time} = \frac{\triangle B}{time}$ we divide the rates in part a and b in half to get .0188 M/s from 0 to 10 seconds and .025 M/s for the estimated instantaneous rate at 15s.

Answer

(a) average rate, 0 − 10 s = 0.0375 mol L^{-1} s^{-1}; average rate, 12 − 18 s = 0.0225 mol L^{-1} s^{-1}; (b) instantaneous rate, 15 s = 0.0500 mol L^{-1} s^{-1}; (c) average rate for B formation = 0.0188 mol L^{-1} s^{-1}; instantaneous rate for B formation = 0.0250 mol L^{-1} s^{-1}

3.E.1.6: Q12.1.6

Consider the following reaction in aqueous solution:

$$5\,\mathrm{Br^-}(aq) + \mathrm{BrO_3^-}(aq) + 6\,\mathrm{H^+}(aq) \longrightarrow 3\,\mathrm{Br_2}(aq) + 3\,\mathrm{H_2O}(l)$$

If the rate of disappearance of Br$^-$(*aq*) at a particular moment during the reaction is 3.5 × 10^{-4} $M\ s^{-1}$, what is the rate of appearance of Br_2(*aq*) at that moment?

Solution

Step 1. Define the rate of the reaction.

Recall:

For the general reaction: aA + bB → cC+ dD

$$rate = -\frac{\Delta[A]}{a\Delta t} = -\frac{\Delta[B]}{b\Delta t} = \frac{\Delta[C]}{c\Delta t} = \frac{\Delta[D]}{d\Delta t}$$

So, for the reaction: $5Br^-(aq) + BrO_3^-(aq) + 6H^+ \rightarrow 3Br_2(aq) + 3H_2O(l)$

The rate would be: $rate = -\frac{\Delta[Br^-]}{5\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{\Delta[H^+]}{6\Delta t} = \frac{\Delta[Br_2]}{3\Delta t} = \frac{H_2O}{3\Delta t}$

Step 2. Since we are given the rate for the disappearance of Br^{-}(aq) is $3.5x10^{-}4Ms^{-1}$, and we want to find the rate of appearance of Br_2(aq). Therefore we set the two rates equal to each other.

$$rate = -\frac{\Delta[Br^{-}]}{5\Delta t} = \frac{\Delta[Br_2]}{3\Delta t}$$

$$\text{And,} -\frac{\Delta[Br^{-}]}{\Delta t} = -3.5x10^{-4}Ms^{-1}$$

$$\text{So, } 3.5x10^{-4}Ms^{-1} = \frac{5}{3}\frac{\Delta[Br_2]}{\Delta t}$$

Step 3. Now solve the equation.

$$\frac{(3.5x10^{-4})(3)}{5} = \frac{\Delta[Br_2]}{\Delta t}$$

$$\frac{\Delta[Br_2]}{\Delta t} = 2.1x10^{-4}Ms^{-1}$$

Answer

$$\frac{\Delta[Br_2]}{\Delta t} = 2.1x10^{-4}Ms^{-1}$$

3.E.2: 12.2: Factors Affecting Reaction Rates

3.E.2.1: Q12.2.1

Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

Solution

Molarity of Hydrochloric Acid

- Reaction rates are affected by the frequency at which molecules collide. High Molarity=High Concentration which means more molecules are available to collide thus a faster reaction that one with a low molarity of HCl at a fixed volume.

Temperature of Solution

- Higher temperatures increase the rate of reaction because molecules move faster thus colliding more frequently
- increasing temperatures allows for more particles to move past activation energy barrier to start the reaction

Size of pieces of Magnesium

- reaction rate is dependent on solid reactant size; smaller pieces increases the chance of collision because they enable a greater surface area thus faster reaction rate

3.E.2.2: Q12.2.2

Go to the PhET Reactions & Rates interactive. Use the Single Collision tab to represent how the collision between monatomic oxygen (O) and carbon monoxide (CO) results in the breaking of one bond and the formation of another. Pull back on the red plunger to release the atom and observe the results. Then, click on “Reload Launcher” and change to “Angled shot” to see the difference.

a. What happens when the angle of the collision is changed?
b. Explain how this is relevant to rate of reaction.

Solution

According to the collision theory, there are many factors that cause a reaction to happen, with three of the factors being how often the molecules or atoms collide, the molecules' or atoms' orientations, and if there is sufficient energy for the reaction to happen. So, if the angle of the plunger is changed, the atom that is shot (a lone Oxygen atom in this case) will hit the other molecule (CO in this case) at a different spot and at a different angle, therefore changing the orientation and the number of proper collisions will most likely not cause for a reaction to happen. Thanks to the simulation, we can see that this is true: depending on the angle selected, the atom may take a long time to collide with the molecule and, when a collision does occur, it may not result in the breaking of the bond and the forming of the other (no reaction happens).

In this particular case, the rate of the reaction will decrease because, by changing the angle, the molecules or atoms won't collide with the correct orientation or as often with the correct orientation.

3.E.2.3: Q12.2.3

In the PhET Reactions & Rates interactive, use the “Many Collisions” tab to observe how multiple atoms and molecules interact under varying conditions. Select a molecule to pump into the chamber. Set the initial temperature and select the current amounts of each reactant. Select “Show bonds” under Options. How is the rate of the reaction affected by concentration and temperature?

3.E.2.4: S12.2.3

Based on the Collision Theory, a reaction will only occur if the molecules collide with proper orientation and with sufficient energy required for the reaction to occur. The minimum energy the molecules must collide with is called the activation energy (energy of transition state).

Increasing the concentration of reactants increases the probability that reactants will collide in the correct orientation since there are more reactants in the same volume of space. Therefore, increasing the concentration of reactants would increase the rate of the reaction. Decreasing the concentration of reactants would decrease the rate of reaction because the overall number of possible collisions would decrease.

Temperature is directly related the the kinetic energy of molecules and activation energy E_a is the minimum energy required for a reaction to occur and doesn't change for a reaction. Increasing the temperature increases the kinetic energy of the reactants meaning the reactants will move faster and collide with each other more frequently. Therefore, increasing the temperature increase the rate of the reaction. Decreasing the temperature decreases the rate of reaction since the molecules will have less kinetic energy, move slower, and therefore collide with each other less frequently.

3.E.2.5: Q12.2.4

In the PhET Reactions & Rates interactive, on the Many Collisions tab, set up a simulation with 15 molecules of A and 10 molecules of BC. Select “Show Bonds” under Options.

a. Leave the Initial Temperature at the default setting. Observe the reaction. Is the rate of reaction fast or slow?
b. Click “Pause” and then “Reset All,” and then enter 15 molecules of A and 10 molecules of BC once again. Select “Show Bonds” under Options. This time, increase the initial temperature until, on the graph, the total average energy line is completely above the potential energy curve. Describe what happens to the reaction.

Solution

a. On the simulation, we select the default setting and the reaction A+BC. In the default setting, we see frequent collisions, a low initial temperature, and a total average energy lower than the energy of activation. The collision theory states that the rate of a reaction is directly proportional to (the fraction of molecules with required orientation), (fractions of collisions with required energy), and (collision frequency). Although we see moving and frequently colliding reactants, the rate of the forward reaction is actually slow because it takes a long time for the products, AB and C, to start appearing. This is mainly because the fractions of collisions with required energy is low, coming from the average energy of the molecules being lower than the energy of activation.

b. The reaction proceeds at an even faster rate. Again, the collision theory states that the rate of a reaction is directly proportional to (the fraction of molecules with required orientation), (fractions of collisions with required energy), and (collision frequency). Because molecules have a higher amount of energy, they have more kinetic energy. With an increased kinetic energy, the molecules not only collide more but also increase in the fraction of collision. However, the forward reaction and the backward reaction both proceed at a fast rate, so both happen almost simultaneously. It takes a shorter time for both reactions to happen. With both of the reactions adding up together overall, there is eventually a state of equilibrium. The process at which equilibrium is reached, however, is faster. Therefore, the amount of products of A+BC stays the same after a while.

3.E.3: 12.3: Rate Laws

3.E.3.1: Q12.3.1

How do the rate of a reaction and its rate constant differ?

3.E.3.2: S12.3.1

The rate of a reaction or reaction rate is the change in the concentration of either the reactant or the product over a period of time. If the concentrations change, the rate also changes.

Rate for A → B:

$$rate = \frac{\Delta[B]}{\Delta t} = -\frac{\Delta[A]}{\Delta t}$$

The rate constant (k) is a proportionality constant that relates the reaction rates to reactants. If the concentrations change, the rate constant does not change.

For a reaction with the general equation: $aA + bB \rightarrow cC + dD$

the experimentally determined rate law usually has the following form:

$$rate = k[A]^m[B]^n$$

3.E.3.3: Q12.3.2

Doubling the concentration of a reactant increases the rate of a reaction four times. With this knowledge, answer the following questions:

a. What is the order of the reaction with respect to that reactant?
b. Tripling the concentration of a different reactant increases the rate of a reaction three times. What is the order of the reaction with respect to that reactant?

Solution

(a) 2; (b) 1

3.E.3.4: Q12.3.3

Tripling the concentration of a reactant increases the rate of a reaction nine times. With this knowledge, answer the following questions:

a. What is the order of the reaction with respect to that reactant?
b. Increasing the concentration of a reactant by a factor of four increases the rate of a reaction four times. What is the order of the reaction with respect to that reactant?

3.E.3.5: Q12.3.4

How much and in what direction will each of the following affect the rate of the reaction: $\mathrm{CO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$ if the rate law for the reaction is $\text{rate} = k[\mathrm{NO_2}]^2$?

a. Decreasing the pressure of NO_2 from 0.50 atm to 0.250 atm.
b. Increasing the concentration of CO from 0.01 *M* to 0.03 *M*.

Solution

(a) The process reduces the rate by a factor of 4. (b) Since CO does not appear in the rate law, the rate is not affected.

3.E.3.6: Q12.3.5

How will each of the following affect the rate of the reaction: $\mathrm{CO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$ if the rate law for the reaction is $\text{rate} = k[\mathrm{NO_2}][\mathrm{CO}]$?

a. Increasing the pressure of NO_2 from 0.1 atm to 0.3 atm
b. Increasing the concentration of CO from 0.02 *M* to 0.06 *M*.

3.E.3.7: Q12.3.6

Regular flights of supersonic aircraft in the stratosphere are of concern because such aircraft produce nitric oxide, NO, as a byproduct in the exhaust of their engines. Nitric oxide reacts with ozone, and it has been suggested that this could contribute to depletion of the ozone layer. The reaction $\mathrm{NO} + \mathrm{O_3} \longrightarrow \mathrm{NO_2} + \mathrm{O_2}$ is first order with respect to both NO and O_3 with a rate constant of 2.20×10^{7} L/mol/s. What is the instantaneous rate of disappearance of NO when [NO] = 3.3×10^{-6} *M* and [O_3] = 5.9×10^{-7} *M*?

Solution

4.3×10^{-5} mol/L/s

3.E.3.8: Q12.3.7

Radioactive phosphorus is used in the study of biochemical reaction mechanisms because phosphorus atoms are components of many biochemical molecules. The location of the phosphorus (and the location of the molecule it is bound in) can be detected from the electrons (beta particles) it produces:

$$^{32}_{15}\mathrm{P} \longrightarrow ^{32}_{16}\mathrm{S} + \mathrm{e}^{-}$$

Rate = $4.85 \times 10^{-2}\ \mathrm{day}^{-1}\ [^{32}\mathrm{P}]$

What is the instantaneous rate of production of electrons in a sample with a phosphorus concentration of 0.0033 *M*?

3.E.3.9: Q12.3.8

The rate constant for the radioactive decay of ^{14}C is 1.21×10^{-4} year^{-1}. The products of the decay are nitrogen atoms and electrons (beta particles):

$$^{6}_{14}\mathrm{C} \longrightarrow ^{6}_{14}\mathrm{N} + \mathrm{e}^{-}$$

$$\mathrm{rate} = k[^{6}_{14}\mathrm{C}]$$

What is the instantaneous rate of production of N atoms in a sample with a carbon-14 content of 6.5×10^{-9} *M*?

Solution

7.9×10^{-13} mol/L/year

3.E.3.10: Q12.3.9

What is the instantaneous rate of production of N atoms Q12.3.8 in a sample with a carbon-14 content of 1.5×10^{-9} *M*?

3.E.3.11: Q12.3.10

The decomposition of acetaldehyde is a second order reaction with a rate constant of 4.71×10^{-8} L/mol/s. What is the instantaneous rate of decomposition of acetaldehyde in a solution with a concentration of 5.55×10^{-4} *M*?

3.E.3.12: Q12.3.11

Alcohol is removed from the bloodstream by a series of metabolic reactions. The first reaction produces acetaldehyde; then other products are formed. The following data have been determined for the rate at which alcohol is removed from the blood of an average male, although individual rates can vary by 25–30%. Women metabolize alcohol a little more slowly than men:

[C_2H_5OH] (*M*)	4.4×10^{-2}	3.3×10^{-2}	2.2×10^{-2}
Rate (mol/L/h)	2.0×10^{-2}	2.0×10^{-2}	2.0×10^{-2}

Determine the rate equation, the rate constant, and the overall order for this reaction.

Solution

rate = *k*; *k* = 2.0×10^{-2} mol/L/h (about 0.9 g/L/h for the average male); The reaction is zero order.

3.E.3.13: Q12.3.12

Under certain conditions the decomposition of ammonia on a metal surface gives the following data:

[NH_3] (*M*)	1.0×10^{-3}	2.0×10^{-3}	3.0×10^{-3}
Rate (mol/L/h^1)	1.5×10^{-6}	1.5×10^{-6}	1.5×10^{-6}

Determine the rate equation, the rate constant, and the overall order for this reaction.

3.E.3.14: Q12.3.13

Nitrosyl chloride, NOCl, decomposes to NO and Cl_2.

$$2\,\mathrm{NOCl}(g) \longrightarrow 2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g)$$

Determine the rate equation, the rate constant, and the overall order for this reaction from the following data:

[NOCl] (*M*)	0.10	0.20	0.30
Rate (mol/L/h)	8.0×10^{-10}	3.2×10^{-9}	7.2×10^{-9}

Solution

Before we can figure out the rate constant first we must first determine the basic rate equation and rate order. The basic rate equation for this reaction, where n is the rate order of NOCl and k is the rate constant, is

$$rate = k[NOCl]^n$$

since NOCl is the reactant in the reaction.

In order to figure out the order of the reaction we must find the order of [NOCl] as it is the only reactant in the reaction. To do this we must examine how the rate of the reaction changes as the concentration of NOCl changes.

As [NOCl] doubles in concentration from 0.10 M to 0.20 M the rate goes from 8.0 x 10^{-10} to 3.2 x 10^{-9}

(3.2 x 10^{-9}(mol/L/h))/(8.0 x 10^{-10}(mol/L/h)) = 4

so we conclude that as [NOCl] doubles, the rate goes up by 4. Since 2^2= 4 we can say that the order of [NOCl] is 2 so our updated rate law is

$$rate = k[NOCl]^2$$

Now that we have the order, we can substitute the first experimental values from the given table to find the rate constant, k

(8.0 x 10^{-10}(mol/L/h)) = k(0.10 M)^2 so

$$k = \frac{8.0 \times 10^{-10}}{(0.10\,M)^2} = 8 \times 10^{-8} M^{-1} sec^{-1}$$

We were able to find the units of k using rate order, when the rate order is 2 units of k are M^{-1} x sec^{-1}

So the rate equation is: rate = k[NOCl]^2, it is second order, and k = 8 x 10^{-8} M^{-1} x sec^{-1}

Overall rate law :

$$rate = \underbrace{(8 \times 10^{-8})}_{1/(\mathrm{M\,x\,sec})} [NOCl]^2$$

Answer

rate = *k*[NOCl]^2; *k* = 8.0 × 10^{-8} L/mol/s; second order

3.E.3.15: Q12.3.14

From the following data, determine the rate equation, the rate constant, and the order with respect to *A* for the reaction $A \longrightarrow 2C$.

[*A*] (*M*)	1.33×10^{-2}	2.66×10^{-2}	3.99×10^{-2}
Rate (mol/L/h)	3.80×10^{-7}	1.52×10^{-6}	3.42×10^{-6}

Solution

A. Using the experimental data, we can compare the effects of changing [A] on the rate of reaction by relating ratios of [A] to ratios of rates

$$\frac{2.66\times 10^{-2}}{1.33\times 10^{-2}}=2$$

and

$$\frac{1.52\times 10^{-6}}{3.8\times 10^{-7}}=4$$

B. From this we know that doubling the concentration of A will result in quadrupling the rate of reaction. The order of this reaction is 2.

C. We can now write the rate equation since we know the order:

$$rate=k[A]^2$$

D. By plugging in one set of experimental data into our rate equation we can solve for the rate constant, k:

$$3.8\times 10^{-7}=k\times(1.33\times 10^{-2})^2$$

$$k=\frac{3.8\times 10^{-7}}{1.769\times 10^{-4}}$$

$$k=.00215M^{-1}s^{-1}$$

Answer

$k=.00215M^{-1}s^{-1}$

2nd Order

3.E.3.16: Q12.3.15

Nitrogen(II) oxide reacts with chlorine according to the equation:

$$2\,\mathrm{NO}(g)+\mathrm{Cl_2}(g)\longrightarrow 2\,\mathrm{NOCl}(g)$$

The following initial rates of reaction have been observed for certain reactant concentrations:

[NO] (mol/L^1)	[Cl_2] (mol/L)	Rate (mol/L/h)
0.50	0.50	1.14
1.00	0.50	4.56
1.00	1.00	9.12

What is the rate equation that describes the rate's dependence on the concentrations of NO and Cl_2? What is the rate constant? What are the orders with respect to each reactant?

Solution

For the general equation,

$aA+bB\rightarrow cC+dD$

The rate can be written as

$rate=k[A]^m[B]^n$ where k is the rate constant, and m and n are the reaction orders.

For our equation

$2NO(g)+Cl_2(g)\rightarrow 2NOCl(g)$

the $rate=k[NO]^m[Cl_2]^n$

Now, we need to find the reaction orders. Reaction orders can only be found through experimental values. We can compare two reactions where one of the reactants has the same concentration for both trials, and solve for the reaction order.

$$\frac{rate_1}{rate_2} = \frac{[NO]_1^m [Cl_2]_1^n}{[NO]_2^m [Cl_2]_2^n}$$

We can use the data in the table provided. If we plug in the values for rows 1 and 2, we see that the values for the concentration of Cl will cancel, leaving just the rates and the concentrations of NO.

$$\frac{1.14}{4.56} = \frac{[0.5]^m}{[1.0]^m}$$

We can now solve for m, and we find that m =2. This means that the reaction order for [NO] is 2.

Now we must find the value of n. To do so, we can use the same equation but with the values from rows 2 and 3. This time, the concentration of NO will cancel out.

$$\frac{4.56}{9.12} = \frac{[0.5]^n}{[1.0]^n}$$

When we solve for n, we find that n = 1. This means that the reaction order for [Cl_2] is 1.

We are one step closer to finishing our rate equation.

$$rate = k[NO]^2[Cl_2]$$

Finally, we can solve for the rate constant. To do this, we can use one of the trials of the experiment, and plug in the values for the rate, and concentrations of reactants, then solve for k.

$$1.14mol/L/h = k[0.5mol/L]^2[0.5mol/L]$$

$$k = 9.12L^2mol^{-2}h^{-1}$$

So, our final rate equation is:

$$rate = (9.12L^2mol^{-2}h^{-1})[NO]^2[Cl_2]$$

*A common mistake is forgetting units. Make sure to track your units throughout the process of determining your rate constant. Be careful because the units will change relative to the reaction order.

Answer

rate = $k[NO]^2[Cl]_2$; k = 9.12 L^2 mol^{-2} h^{-1}; second order in NO; first order in Cl_2

3.E.3.17: Q12.3.17

Hydrogen reacts with nitrogen monoxide to form dinitrogen monoxide (laughing gas) according to the equation:

$$H_2(g) + 2\,NO(g) \longrightarrow N_2O(g) + H_2O(g)$$

Determine the rate equation, the rate constant, and the orders with respect to each reactant from the following data:

[NO] (*M*)	0.30	0.60	0.60
[H_2] (*M*)	0.35	0.35	0.70
Rate (mol/L/s)	2.835×10^{-3}	1.134×10^{-2}	2.268×10^{-2}

Solution

Determine the rate equation, the rate constant, and the orders with respect to each reactant.

The rate constant and the orders can be determined through the differential rate law. The general form of the differential rate law is given below:

aA + bB + cC ==> products

$$rate = - d[A]/dt = k[A]^n[B]^m[C]^p$$

where A, B, and C are the concentrations of the reactants, k is the rate constant, and n,m, and p refer to the order of each reactant.

To find the orders of each reactant, we see that when [NO] doubles but $[H_2]$ doesn't change, the rate quadruples, meaning that [NO] is a second order reaction ($[NO]^2$). When $[H_2]$ doubles but [NO] doesn't change, the rate doubles, meaning that $[H_2]$ is a first order reaction. So the rate law would look something like this:

$$\text{Rate} = k[NO]^2[H_2]$$

We can use this rate law to determine the value of the rate constant. Plug in the data for reactant concentration and rate from one of the trials to solve for k the rate constant. In this case, we chose to use the data from trial 1 from the second column of the data table.

$$2.835\text{x}10^{-3} = k[0.3]^2[0.35]$$

$$k = .09\ M^{-2}/s^{-1}$$

3.E.3.18: Q12.3.18

For the reaction $A \longrightarrow B+C$, the following data were obtained at 30 °C:

[A] (*M*)	0.230	0.356	0.557
Rate (mol/L/s)	4.17×10^{-4}	9.99×10^{-4}	2.44×10^{-3}

a. What is the order of the reaction with respect to [*A*], and what is the rate equation?
b. What is the rate constant?

Solution

1. The rate equation for an n order reaction is given as $\frac{dr}{dt} = k[A]^n$. Where $[A]$ is the concentration in M, and $\frac{dr}{dt}$ is the rate in M/s.

We can then use each set of data points, plug its values into the rate equation and solve for n. Note you can use any of the data points as long as the concentration corresponds to its rate.

Rate equation 1: $4.17 \times 10^{-4} = k[0.230]^n$

Rate equation 2: $9.99 \times 10^{-4} = k[0.356]^n$

We divide Rate equation 1 by Rate equation 2 in order to cancel out k, the rate constant.

$$\frac{4.17 \times 10^{-4}}{9.99 \times 10^{-4}} = \frac{k[0.230]^n}{k[0.356]^n}$$

$$0.417 = 0.646^n$$

Now the only unknown we have is n. Using logarithm rules one can solve for it.

$$ln\ 0.417 = n \cdot ln\ 0.646$$

$$\frac{ln\ 0.417}{ln\ 0.646} = n = 2$$

The rate equation is second order with respect to A and is written as $\frac{dr}{dt} = k[A]^2$.

2. We can solve for k by plugging in any data point into our rate equation $\frac{dr}{dt} = k[A]^2$.

Using the first data points for instance $[A] = 0.230\ \frac{mol}{L}$ and $\frac{dr}{dt} = 4.17 \times 10^{-4}\ \frac{mol}{L \cdot s}$] we get the equation $4.17 \times 10^{-4}\ \frac{mol}{L \cdot s} = k[0.230\ \frac{mol}{L}]^2$

Which solves for $k = 7.88 \times 10^{-3}\ \frac{L}{mol \cdot s}$

Since we know this is a second order reaction the appropriate units for k can also be written as $\frac{1}{M \cdot s}$

Answer

(a) The rate equation is second order in A and is written as rate = $k[A]^2$. (b) $k = 7.88 \times 10^{-13}$ L mol^{-1} s^{-1}

3.E.3.19: Q12.3.19

For the reaction $Q \longrightarrow W + X$, the following data were obtained at 30 °C:

$[Q]_{initial}$ (M)	0.170	0.212	0.357
Rate (mol/L/s)	6.68×10^{-3}	1.04×10^{-2}	2.94×10^{-2}

a. What is the order of the reaction with respect to [Q], and what is the rate equation?
b. What is the rate constant?

Solution

What is the order of the reaction with respect to [Q], and what is the rate equation?

- Order reaction: 2 because when you use the ratio trial 3:2, it will look like this:
- $(\frac{2.94 * 10^{-2}}{1.04 * 10^{-2}}) = (\frac{0.357^x}{0.212^x})$
- $2.82 = 1.7^x$
- x = 2 so the order of reaction is 2
- Rate reaction equation: Rate=k$[Q]^2$

What is the rate constant?

- To find the rate constant (k) simply plug and calculate one of the trials into the rate equation
- $1.04 \text{ x } 10^{-2}$=k$[0.212]^2$
- k=0.231 $M^{-1}s^{-1}$

Answer

Order: 2

k=0.231 $M^{-1}s^{-1}$

3.E.3.20: Q12.3.20

The rate constant for the first-order decomposition at 45 °C of dinitrogen pentoxide, N_2O_5, dissolved in chloroform, $CHCl_3$, is 6.2 × 10^{-4} min^{-1}.

$$2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$$

What is the rate of the reaction when $[N_2O_5]$ = 0.40 M?

Solution

Step 1: The first step is to write the rate law. We know the general formula for for a first-order rate law. It is as follows: Rate=k[A]

Step 2: We now plug in $[N_2O_5]$ in for [A] in our general rate law. We also plug in our rate constant (k), which was given to us. Now our equation looks as follows:

Rate=$(6.2\text{x}10^{-4}\text{ min}^{-1})[N_2O_5]$

Step 3: We now plug in our given molarity. $[N_2O_5]$=0.4 M. Now our equation looks as follows:

Rate=$(6.2\text{x}10^{-4}\text{ min}^{-1})$(0.4 M)

Step 4: We now solve our equation. Rate=$(6.2\text{x}10^{-4}\text{ min}^{-1})$(0.4 M)= $2.48\text{x}10^{-4}$ M/min.
Step 5: Use significant figures and unit conversion to round $2.48\text{x}10^{-4}$ M/min to 2.5 × 10^{-4} (moles)$L^{-1}min^{-1}$

Answer

(a) 2.5 × 10^{-4} mol/L/min

3.E.3.21: Q12.3.21

The annual production of HNO_3 in 2013 was 60 million metric tons Most of that was prepared by the following sequence of reactions, each run in a separate reaction vessel.

a. $4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$
b. $2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$
c. $3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g)$

The first reaction is run by burning ammonia in air over a platinum catalyst. This reaction is fast. The reaction in equation (c) is also fast. The second reaction limits the rate at which nitric acid can be prepared from ammonia. If equation (b) is second order in NO and first order in O_2, what is the rate of formation of NO_2 when the oxygen concentration is 0.50 *M* and the nitric oxide concentration is 0.75 *M*? The rate constant for the reaction is 5.8×10^{-6} $L^2/mol^2/s$.

Solution

To determine the rate law for an equation we need to look at its slow step. Since both equation a and c are fast, equation b can be considered the slow step of the reaction. The slow step is also considered the rate determining step of the system.

Hence, The rate determining step is the second step because it's the slow step.

rate of production of $NO_2 = k[A]^m[B]^n$

$rate = k[NO]^2[O_2]^1\ M/s$

$rate = (5.8 * 10^{-6})[0.75]^2[0.5]^1\ M/s$

$rate = 1.6 * 10^{-6}\ M/s$

Answer

$rate = 1.6 * 10^{-6}\ M/s$

3.E.3.22: Q12.3.22

The following data have been determined for the reaction:

$$I^- + OCl^- \longrightarrow IO^- + Cl^-$$

	1	**2**	**3**
$[I^-]_{initial}$ (*M*)	0.10	0.20	0.30
$[OCl^-]_{initial}$ (*M*)	0.050	0.050	0.010
Rate (mol/L/s)	3.05×10^{-4}	6.20×10^{-4}	1.83×10^{-4}

Determine the rate equation and the rate constant for this reaction.

Solution

Using the reactants, we can form the rate law of the reaction: $$ r=k[OCl^-]^n[I^-]^m \]

From there, we need to use the data to determine the order of both $[OCl^-]$ and $[I^-]$. In doing so, we need to compare r_1 to r_2 such that:

$$\frac{r_1}{r_2} = \frac{(0.10^m)(0.050^n)}{(0.20^m)(0.050^n)} = \frac{3.05 \times 10^{-4}}{6.20 \times 10^{-4}} \tag{3.E.3}$$

$$0.5^m = 0.5 \tag{3.E.4}$$

$$m = 1 \tag{3.E.5}$$

We can "cross out" the concentration of $[OCl^-]$ because it has the same concentration in both of the trials used.

Now that we know m ($[I^-]$) has a first order of 1.

We cannot "cross out" $[I^-]$ to find $[OCl^-]$ because no two trials have the same concentration. In order to solve for n we will plug in 1 for m.

$$\frac{r_1}{r_3} = \frac{(0.10^1)(0.050^n)}{(0.30^1)(0.010^n)} = \frac{3.05\times10^{-4}}{1.83\times10^{-4}} \tag{3.E.6}$$

$$\frac{1}{3}(5^n) = 1.6666667 \tag{3.E.7}$$

$$5^n = 5 \tag{3.E.8}$$

$$n = 1 \tag{3.E.9}$$

Since we know that orders of both n and m are equal to one, we can not substitute them into the rate law equation along with the respective concentrations (from either the first, second, or third reaction) and solve for the rate constant, k.

$$r = k[OCl^-]^n[I^-]^m \tag{3.E.10}$$

$$3.05*10^{-4} = k[0.05]^1[0.10]^1 \tag{3.E.11}$$

$$k = 6.1*10^{-2}\frac{L}{mol\times s} \tag{3.E.12}$$

Thus the overall rate law is: $$ r = (6.1 * 10^{-2} \frac {L}{mol \times s})[OCl^-][I^-] \]

The units for K depend on the overall order of the reaction. To find the overall order we add m and n together. By doing this we find an overall order of 2. This is why the units for K are $$ \frac {L}{mol \times s} \]

Answer

rate = k[I$^-$][OCl^{-1}]; k = 6.1 × 10^{-2} L mol $^{-1}$ s^{-1}

3.E.3.23: Q12.3.23

In the reaction

$$2NO + Cl_2 \rightarrow 2NOCl$$

the reactants and products are gases at the temperature of the reaction. The following rate data were measured for three experiments:

Initial p{NO}	Initial p{Cl_2}	Initial rate
(atm)	(atm)	(moles of A consumed atm sec^{-1})
0.50	0.50	5.1 x 10^{-3}
1.0	1.0	4.0 x 10^{-2}
0.50	1.0	1.0 x 10^{-2}

a. From these data, write the rate equation for this gas reaction. What order is the reaction in NO, Cl_2, and overall?
b. Calculate the specific rate constant for this reaction.

Solution

a. The rate equation can be determined by designing experiments that measure the concentration(s) of one or more reactants or products as a function of time. For the reaction $A + B \rightarrow products$, for example, we need to determine *k* and the exponents *m* and *n* in the following equation:

$$rate = k[A]^m[B]^n$$

To do this, the initial concentration of B can be kept constant while varying the initial concentration of A and calculating the initial reaction rate. This information would deduce the reaction order with respect to A. The same process can be done to find

the reaction order with respect to B.
In this particular example,

$$\frac{rate_2}{rate_3} = \frac{k[A_2]^m[B_2]^n}{k[A_3]^m[B_3]^n}$$

So taking the values from the table,

$$\frac{4.0 * 10^{-2}}{1.0 * 10^{-2}} = \frac{k[1.0]^m[1.0]^n}{k[0.5]^m[1.0]^n}$$

and by canceling like terms, you are left with

$$\frac{4.0 * 10^{-2}}{1.0 * 10^{-2}} = \frac{[1.0]^m}{[0.5]^m}$$

Now, solve for m

$4 = 2^m \implies m = 2$ Because m=2, the reaction with respect to NO is 2. NO **is second order.**

You can repeat the same process to find n.

$$\frac{rate_3}{rate_1} = \frac{k[A_3]^m[B_3]^n}{k[A_1]^m[B_1]^n}$$

Taking the values from the table,

$$\frac{1.0 * 10^{-2}}{5.1 * 10^{-3}} = \frac{k[0.5]^m[1.0]^n}{k[0.5]^m[0.5]^n}$$

and by canceling like terms, you are left with

$$\frac{1.0 * 10^{-2}}{5.1 * 10^{-3}} = \frac{[1.0]^n}{[0.5]^n}$$

Now this time, solve for n

$2 = 2^n \implies n = 1$

Because n=1, the reaction with respect to Cl_2 is 1. Cl_2 **is first order.**

So the rate equation is

$$rate = k[NO]^2[Cl_2]^1$$

To find the overall rate order, you simply add the orders together. Second order + first order makes the **overall reaction third order.**

b. The rate constant is calculated by inserting the data from any row of the table into the experimentally determined rate law and solving for k. For a third order reaction, the units of k are $frac1atm^2 * sec$. Using Experiment 1,

$$rate = k[NO]^2[Cl_2]^1 \implies 5.1 * 10^{-3} \frac{atm}{sec} = k[0.5matm]^2[0.5atm]^1$$

$$k = 0.0408 \frac{1}{atm^2 * sec}$$

Answer

NO is second order.

Cl_2 is first order.

Overall reaction order is three.

b)

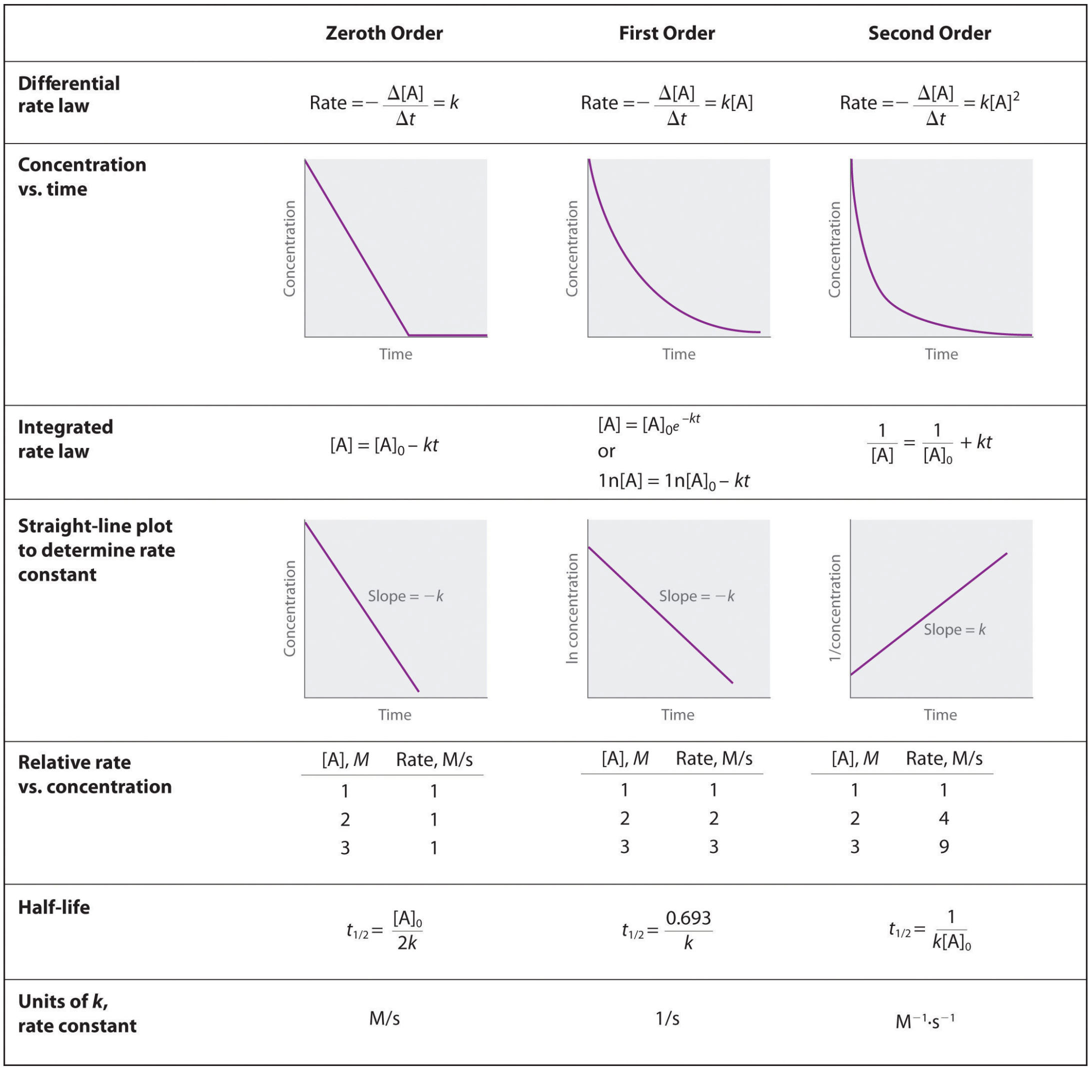
$k = 0.0408\ atm^{-2} * sec^{-1}$

3.E.4: 12.4: Integrated Rate Laws

3.E.4.1: Q12.4.1

Describe how graphical methods can be used to determine the order of a reaction and its rate constant from a series of data that includes the concentration of *A* at varying times.

Solution



	Zeroth Order	First Order	Second Order
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$
Concentration vs. time	Concentration Time	Concentration Time	Concentration Time
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0e^{-kt}$ or $1n[A] = 1n[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Straight-line plot to determine rate constant	Concentration Slope = −k Time	ln concentration Slope = −k Time	1/concentration Slope = k Time
Relative rate vs. concentration	[A], M / Rate, M/s 1 / 1 2 / 1 3 / 1	[A], M / Rate, M/s 1 / 1 2 / 2 3 / 3	[A], M / Rate, M/s 1 / 1 2 / 4 3 / 9
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$
Units of k, rate constant	M/s	1/s	$M^{-1}\cdot s^{-1}$

To determine the order of a reaction when given the data series, one must graph the data how it is, graph it as natural log of [A], and graph it as 1/[A]. Whichever method yields a straight line will determine the order. Respective of the methods of graphing above, if a straight line is yielded by the first graphing method its a 0 order, if by the second method it's a 1st order, and the third graphing method its a 2nd order. When the order of the graph is known, a series of equations, given in the above image, can be used with the various points on the graph to determine the value of k. We can see that we need an initial value of A and a final value of A, and both of these would be given by the data.

Zeroth order when plotting initial concentrating versus final concentration you have a negative linear slope.

$$[A] = [A]_0 - kt$$

First order when plotting ln[initial concentration] versus ln[final concentration] you have a negative linear slope.

$$\ln[A] = \ln[A]_0 - kt$$

Second order when plotting the 1/[initial concentration] versus 1/[final concentration] you have a positive linear slope.

$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + kt$$

3.E.4.2: Q12.4.2

Use the data provided to graphically determine the order and rate constant of the following reaction: $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$

Time (s)	0	5.00 × 10^3	1.00 × 10^4	1.50 × 10^4	2.50 × 10^4	3.00 × 10^4	4.00 × 10^4

$[SO_2Cl_2]$ (*M*)	0.100	0.0896	0.0802	0.0719	0.0577	0.0517	0.0415

Solution

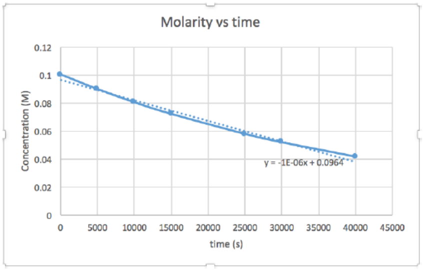
Use the data to graphically determine the order and rate constant of the following reaction.

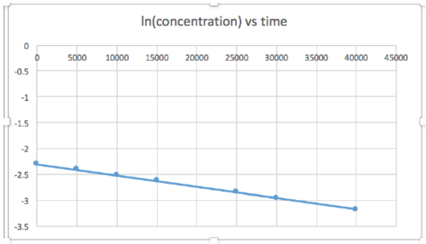
In order to determine the rate law for a reaction from a set of data consisting of concentration (or the values of some function of concentration) versus time, make three graphs of the data based on the integrated rate laws of each order reaction.

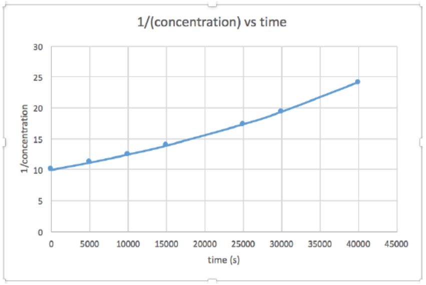
[concentration] versus time (linear for a zero order reaction) ln [concentration] versus time (linear for a 1st order reaction) 1 / [concentration] versus time (linear for a 2nd order reaction)

slope= -2.0×10^{-5}

k = 2.0×10^{-5}





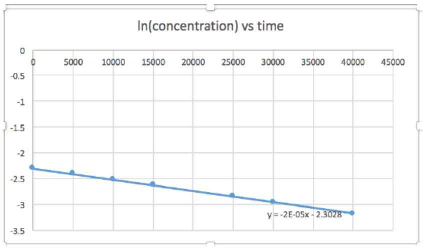


The graph that is linear indicates the order of the reaction. Then, you can find the correct rate equation:

zero order reaction	rate = k	(k = - slope of line)
1st order reaction	rate = k[A]	(k = - slope of line)
2nd order reaction	rate = $k[A]^2$	(k = slope of line)

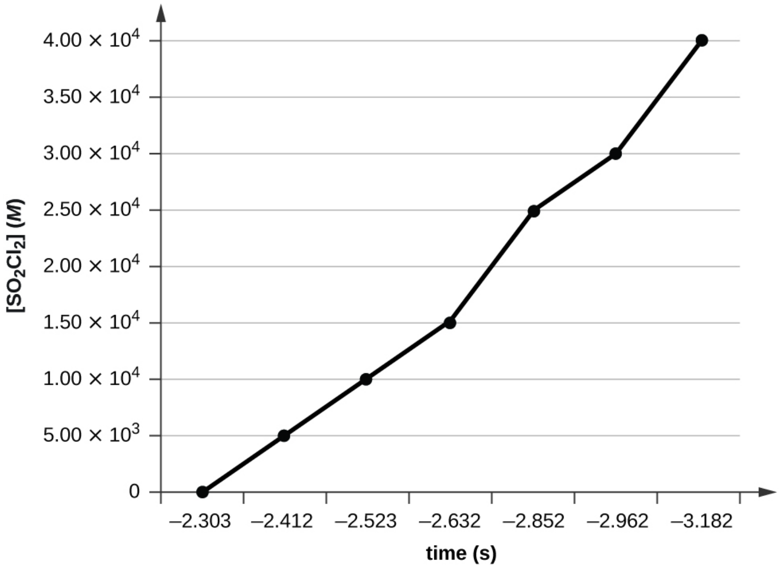
In this graph, ln(concentration) vs time is linear, indicating that the **reaction is first order**.

k=-slope of line



Answer

Plotting a graph of ln[SO_2Cl_2] versus *t* reveals a linear trend; therefore we know this is a first-order reaction:



$k = -2.20 \times 10^5\ s^{-1}$

3.E.4.3: Q12.4.3

Use the data provided in a graphical method to determine the order and rate constant of the following reaction:

$$2P \longrightarrow Q + W$$

Time (s)	9.0	13.0	18.0	22.0	25.0
[P] (*M*)	1.077×10^{-3}	1.068×10^{-3}	1.055×10^{-3}	1.046×10^{-3}	1.039×10^{-3}

Solution

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3.E.4.4: Q12.4.4

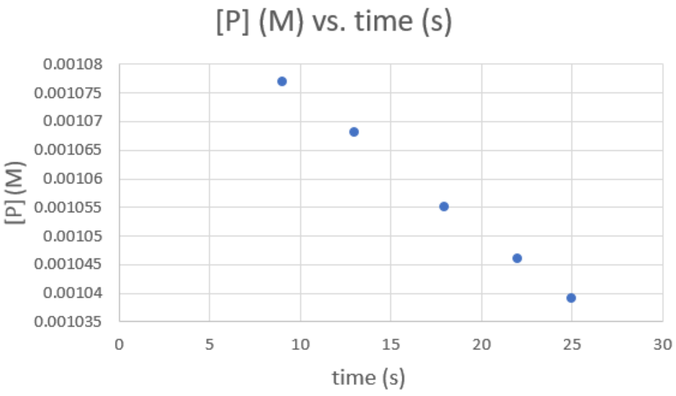
Pure ozone decomposes slowly to oxygen, $2\,O_3(g) \longrightarrow 3\,O_2(g)$. Use the data provided in a graphical method and determine the order and rate constant of the reaction.

Time (h)	0	2.0×10^3	7.6×10^3	1.23×10^4	1.70×10^4	1.70×10^4
[O_3] (*M*)	1.00×10^{-5}	4.98×10^{-6}	2.07×10^{-6}	1.39×10^{-6}	1.22×10^{-6}	1.05×10^{-6}

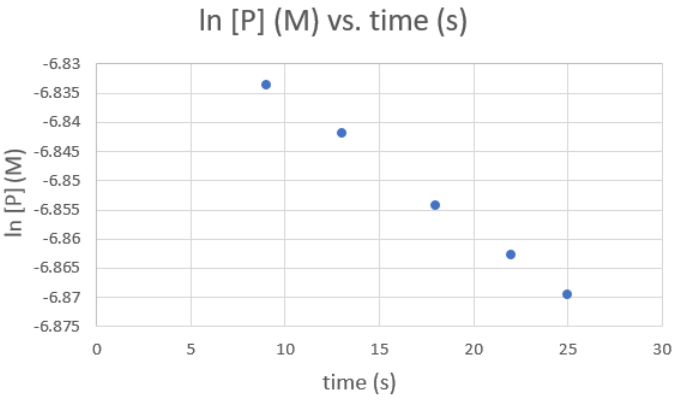
Solution

To determine the order and rate constant, you need to graph the data for zero order, first order, and second order by plotting concentration versus time- [A] vs. time, natural logarithm (ln) of [A] vs. time, and 1/[A] vs. time respectively. The order of the reaction is determined by identifying which of these three graphs produces a straight line. The rate constant *k* is represented by the slope of the graph. The graphs with their respective data values would be

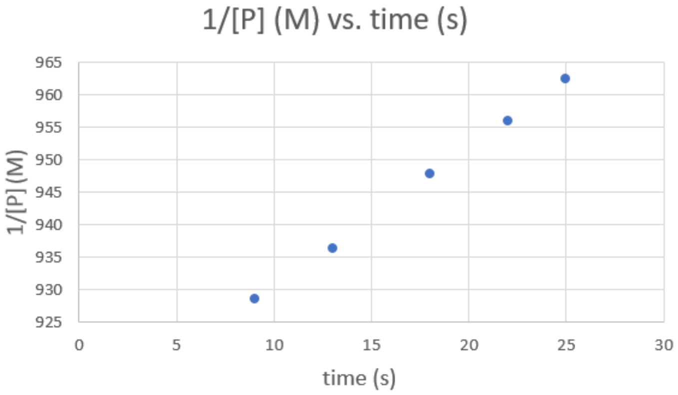
Time (s)	9.0	13.0	18.0	22.0	25.0
[P] (*M*)	1.077 × 10−3	1.068 × 10−3	1.055 × 10−3	1.046 × 10−3	1.039 × 10−3



Time (s)	9.0	13.0	18.0	22.0	25.0
ln [P] (*M*)	-6.83358	-6.84197	-6.85421	-6.86278	-6.8695

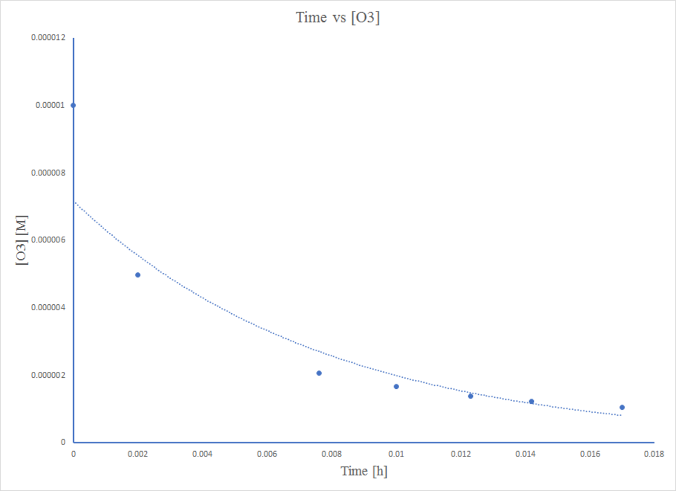


Time (s)	9.0	13.0	18.0	22.0	25.0
1/[P] (*M*)	928.5051	936.3296	947.8673	956.0229	962.4639

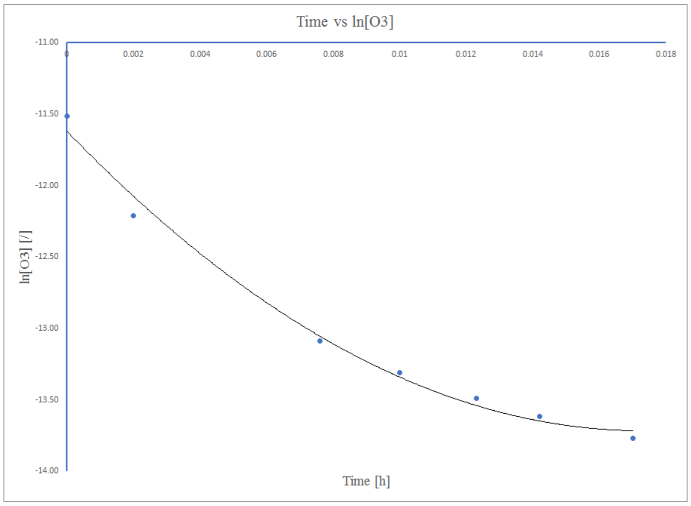


Since each graph yields a straight line **the order and rate constant of the reaction cannot be determined**.

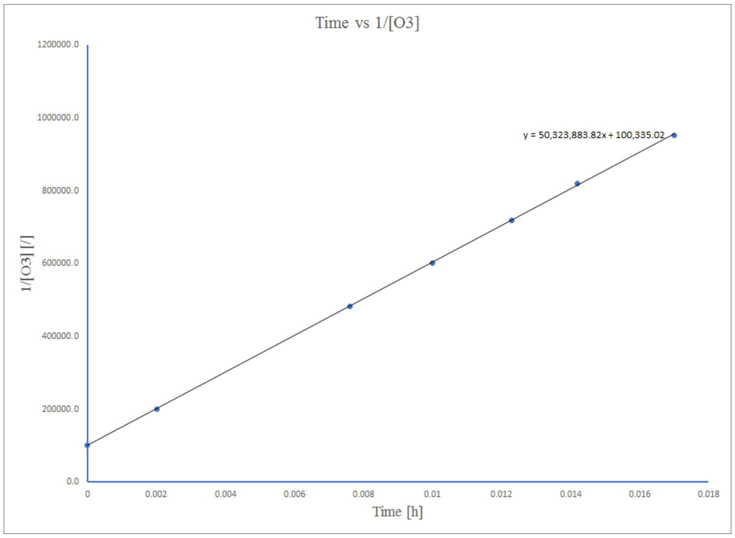
To identify how the concentrations changes a function of time, requires solving the appropriate differential equation (i.e., the differential rate law).
The zero-order rate law predicts in a linear decay of concentration with time
The 1st-order rate law predicts in an exponential decay of concentration with time
The 2nd-order rate law predicts in an reciprocal decay of concentration with time



The plot is not linear, so the reaction is not zero order.



The plot is not linear, so the reaction is not first order.



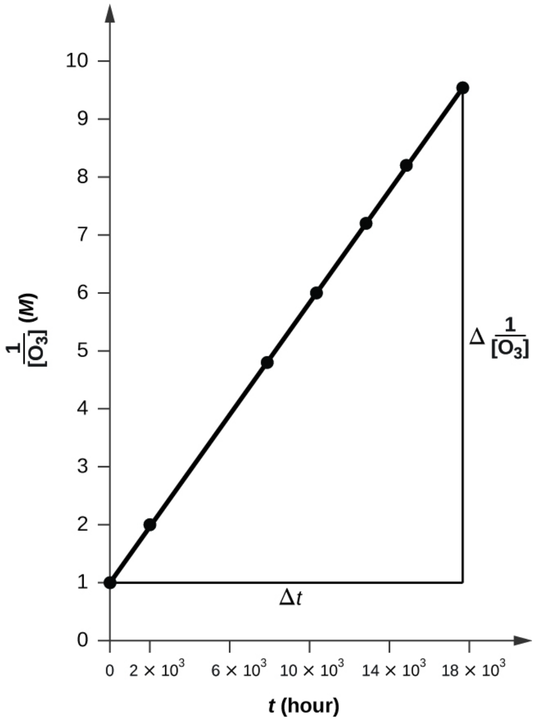
The plot is nicely linear, so the reaction is second order.

To a second order equation, $1/[A] \; = k * t + 1/[A_0]$

Thus, the value of K is the slope of the graph Time vs $\frac{1}{O_3}$,

k = 50.3*10^6 L mol^{-1} h^{-1}

Answer



The plot is nicely linear, so the reaction is second order.

k = 50.1 L mol^{-1} h^{-1}

3.E.4.5: Q12.4.5

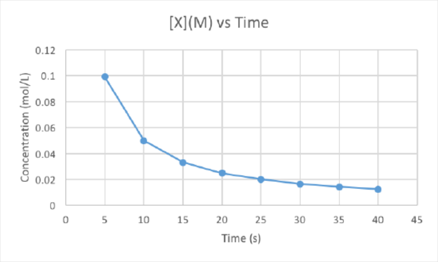
From the given data, use a graphical method to determine the order and rate constant of the following reaction:

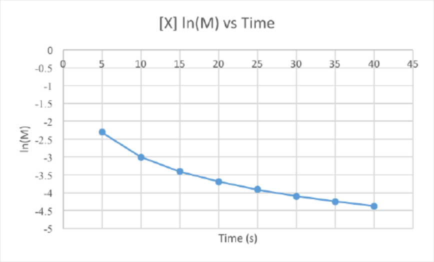
$$2X \longrightarrow Y+Z \tag{3.E.13}$$

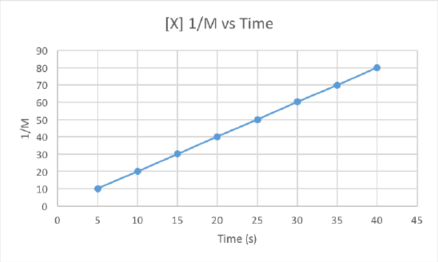
Time (s)	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
[*X*] (*M*)	0.0990	0.0497	0.0332	0.0249	0.0200	0.0166	0.0143	0.0125

Solution

In order to determine the order of the reaction we need to plot the data using three different graphs. All three graphs will have time in seconds as the x-axis, but the y-axis is what will differ. One graph will plot concentration versus time, the second will plot natural log of concentration versus time, and the other will plot 1/concentration versus times. Whichever graph results in a line, we know that must be the order of the reaction. If we get a line using the first graph, it will be zero order, if it is a line for the second graph it will be first order, and if it is a line for the third graph it will be a second order reaction. Now lets plot the data to determine the order.







We can clearly see that the third graph, which plots 1/M versus time, is a straight line while the other two are slightly curved. Therefore, we can determine that the rate of this reaction is second order. This also tells us that the units of the rate constant which should be $M^{-2}s^{-1}$ for a second order reaction.

To determine the rate constant, called k, we simple need to figure out the slope of the third graph since that is the order of this reaction. To find the slope of the line, we take two points and subtract the y values and then divide them by the difference of the x values. This is how to do it:

Use the points (5, 10.101) and (40, 80).

Now use these to get the slop, aka the rate constant: (80-10.101)/(40-5) = 1.997 = k

So the rate constant for this second order reaction is 1.997 $M^{-1}s^{-1}$.

3.E.4.6: Q12.4.6

What is the half-life for the first-order decay of phosphorus-32? $\left({}^{32}_{15}\text{P} \longrightarrow {}^{32}_{16}\text{S} + \text{e}^-\right)$ The rate constant for the decay is 4.85 × 10^{-2} day^{-1}.

Solution

This is a first order reaction, so we can use our half life equation below:

$$t_{1/2} = \frac{0.693}{k}$$

The rate constant is given to us in units per day. All we have to do, is to plug it into the equation.

$$t_{1/2} = \frac{0.693}{4.85 * 10^{-2}}$$
$$= 14.3\ days$$

A12.4.6

14.3 d

3.E.4.7: Q12.4.7

What is the half-life for the first-order decay of carbon-14? $({}^{6}_{14}\mathrm{C} \longrightarrow {}^{7}_{14}\mathrm{N} + \mathrm{e}^{-})$ The rate constant for the decay is 1.21 × 10^{-4} year^{-1}.

Solution

To find the half life, we need to use the first-order half-life equation. All half life reactions undergo first order reactions.

The half-life equation for first order is

$$t_{1/2} = ln2/k$$

with k being the rate constant. The rate constant for carbon-14 was given as $1.21 \times 10^{-4} year^{-1}$.

Plug it in the equation.

$$t_{1/2} = ln2/(1.21 \times 10^{-4} year^{-1})$$

and solve for $t_{1/2}$.

When you calculate it, the half life for carbon-14 is 5.73*10^3

Answer

The half-life for carbon-14 is calculated to be 5.73*10^3

3.E.4.8: Q12.4.8

What is the half-life for the decomposition of NOCl when the concentration of NOCl is 0.15 *M*? The rate constant for this second-order reaction is 8.0 × 10^{-8} L/mol/s.

Solution

The half-life of a reaction, $t_{1/2}$, is the amount of time that is required for a reactant concentration to decrease by half compared to its initial concentration. When solving for the half-life of a reaction, we should first consider the order of reaction to determine it's rate law. In this case, we are told that this reaction is second-order, so we know that the integrated rate law is given as:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Isolating for time, we find that:

$$t_{1/2} = \frac{1}{k[A]_0}$$

Now it is just a matter of substituting the information we have been given to calculate $t_{1/2}$, where the rate constant, k, is equal to 8.0 × 10^{-8} L/mol/s and initial concentration, $[A]_0$, is equal to 0.15*M*:

$$t_{1/2} = \frac{1}{(8.0 \times 10^{-8})(0.15)} = 8.33 \times 10^{7} seconds$$

Answer

8.33 × 10^7 s

3.E.4.9: Q12.4.9

What is the half-life for the decomposition of O_3 when the concentration of O_3 is 2.35×10^{-6} M? The rate constant for this second-order reaction is 50.4 L/mol/h.

Solution

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Since the reaction is second order, its half-life is

$$t_{\frac{1}{2}} = \frac{1}{k[\mathrm{A}]_0}$$

$$t_{1/2} = \frac{1}{(50.4M^{-1}/h)[2.35 \times 10^{-6}M]}$$

So, half-life is 8443 hours.

3.E.4.10: Q12.4.10

The reaction of compound *A* to give compounds *C* and *D* was found to be second-order in *A*. The rate constant for the reaction was determined to be 2.42 L/mol/s. If the initial concentration is 0.500 mol/L, what is the value of $t_{1/2}$?

Solution

As mentioned in the question the reaction of compound *A* will result in the formation of compounds C and D. This reaction was found to be second-order in *A*. Therefore, we should use the second order equation for half-life which relates the rate constant and initial concentrations to the half-life:

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

Since we were given *k* (rate constant) and Initial concentration of A, we have everything needed to calculate the half life of A.

$$k = 0.5\frac{\frac{L}{mol}}{s}$$

$$[A]_0 = 2.42\frac{mol}{L}$$

When we plug in the given information notice that the units cancel out to seconds.

$$t_{\frac{1}{2}} = \frac{1}{\frac{2.42Lmol^{-}}{s}[0.500\frac{mol}{L}]} = 0.826s$$

Answer

0.826 s

3.E.4.11: Q12.4.11

The half-life of a reaction of compound *A* to give compounds *D* and *E* is 8.50 minutes when the initial concentration of *A* is 0.150 mol/L. How long will it take for the concentration to drop to 0.0300 mol/L if the reaction is (a) first order with respect to *A* or (b) second order with respect to *A*?

Solution

Organize the given variables:

(half-life of *A*) $t_{1/2} = 8.50min$
(initial concentration of *A*) $[A]_0 = 0.150mol/L$
(target concentration of *A*) $[A] = 0.0300mol/L$

Find the the rate constant k, using the half-life formulas for each respective order. After finding k, use the integrated rate law respective to each order and the initial and target concentrations of *A* to find the time it took for the concentration to drop.

(a) first order with respect to *A*

(half-life) $t_{1/2} = \frac{ln(2)}{k} = \frac{0.693}{k}$

(rearranged for k) $k = \frac{0.693}{t_{1/2}}$

(plug in $t_{1/2}$ = 8.50 min) $k = \frac{0.693}{8.50min} = 0.0815min^{-1}$

(integrated rate law) $ln[A] = -kt + ln[A]_0$

(rearranged for t) $ln(\frac{[A]}{[A]_0}) = -kt$

$-ln(\frac{[A]}{[A]_0}) = kt$

$ln(\frac{[A]}{[A]_0})^{-1} = kt$

$ln(\frac{[A]_0}{[A]}) = kt$

$t = \frac{ln(\frac{[A]_0}{[A]})}{k}$

(plug in variables) $t = \frac{ln(\frac{0.150mol/L}{0.0300mol/L})}{0.0815min^{-1}} = \frac{ln(5.00)}{0.0815min^{-1}} = 19.7min$

(b) second order with respect to *A*

(half-life) $t_{1/2} = \frac{1}{k[A]_0}$

(rearranged for k) $k = \frac{1}{t_{1/2}[A]_0}$

(plug in variables) $k = \frac{1}{(8.50min)(0.150mol/L)} = \frac{1}{1.275min \cdot mol/L} = 0.784L/mol \cdot min$

(integrated rate law) $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$

(rearranged for t) $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$

$t = \frac{1}{k}(\frac{1}{[A]} - \frac{1}{[A]_0})$

(plug in variables) $t = \frac{1}{0.784L/mol \cdot min}(\frac{1}{0.0300mol/L} - \frac{1}{0.150mol/L}) = \frac{1}{0.784L/mol \cdot min}(\frac{80}{3}L/mol) = 34.0min$

Answer

a) 19.7 min

b) 34.0 min

3.E.4.12: Q12.4.12

Some bacteria are resistant to the antibiotic penicillin because they produce penicillinase, an enzyme with a molecular weight of 3 × 10^4 g/mol that converts penicillin into inactive molecules. Although the kinetics of enzyme-catalyzed reactions can be complex, at low concentrations this reaction can be described by a rate equation that is first order in the catalyst (penicillinase) and that also involves the concentration of penicillin. From the following data: 1.0 L of a solution containing 0.15 µg (0.15 × 10^{-6} g) of penicillinase, determine the order of the reaction with respect to penicillin and the value of the rate constant.

[Penicillin] (*M*)	Rate (mol/L/min)
2.0×10^{-6}	1.0×10^{-10}
3.0×10^{-6}	1.5×10^{-10}
4.0×10^{-6}	2.0×10^{-10}

Solution

The first step is to solve for the order or the reaction. This can be done by setting up two expressions which equate the rate to the rate constant times the molar concentration of penicillin raised to the power of it's order. Once we have both expressions set up, we can divide them to cancel out k (rate constant) and use a basic logarithm to solve for the exponent, which is the order. It will look like this.

$$\text{rate(mol/L/min)}=k[M]^x$$

$$(1.0 \text{ x } 10^{-10})=k[2.0 \text{ x } 10^{-6}]^x$$

$$(1.5 \text{ x } 10^{-10})=k[3.0 \text{ x } 10^{-6}]^x$$

Dividing the two equations results in the expression:

$$(2/3)=(2/3)^x$$

*A single ratio equation can also be set up to solve for the reaction order:

*

$$\frac{rate_1}{rate_2}=\frac{k[Penicillin]_1^x}{k[Penicillin]_2^x}$$

*We then solve for x in a similar fashion.

*

$$\frac{1.0x10^{-10}}{1.5x10^{-10}}=\frac{[2.0x10^{-6}]^x}{[3.0x10^{-6}]^x}$$

We can now use the natural logarithm to solve for x, or simply and intuitively see that in order for the equation to work, **x must be equal to one. Thus, the reaction is of the first order.**

Now that we have the order of the reaction, we can proceed to solve for the value of the rate constant. Substituting x=1 into our first equation yields the expression:

$$(1 \text{ x } 10^{-10})=k[2.0 \text{ x } 10^{-6}]^1$$

$$k=(1 \text{ x } 10^{-10})/(2 \text{ x } 10^{-6})$$

$$k=(5 \text{ x } 10^{-5}) \text{ min}^{-1}$$

We have a unit of min^{-1} because we divided (mol/L/min) by molarity, which is in (mol/L), yielding a unit of min^{-1}.

We were given two important pieces of information to finish the problem. It is stated that the enzyme has a molecular weight of 3×10^4 g/mol, and that we have a one liter solution that contains ($0.15 \text{ x } 10^{-6}$ g) of penicillinase. Dividing the amount of grams by the molecular weight yields **$5 \text{ x } 10^{-12}$ moles**.

$$(0.15 \text{ x } 10^{-6}) \text{ g} / (3 \text{ x } 10^4) \text{ g/mol} = (5 \text{ x } 10^{-12}) \text{ mol}$$

Now that we have the amount of moles, we can divide our rate constant by this value.

$$(5 \text{ x } 10^{-5}) \text{ min}^{-1} / (5 \text{ x } 10^{-12}) \text{ mol} = \mathbf{(1 \text{ x } 10^7) \text{ mol}^{-1} \text{ min}^{-1}}$$

Answer

The reaction is first order with $k = 1.0 \times 10^7 \text{ mol}^{-1} \text{ min}^{-1}$

3.E.4.13: Q12.4.13

Both technetium-99 and thallium-201 are used to image heart muscle in patients with suspected heart problems. The half-lives are 6 h and 73 h, respectively. What percent of the radioactivity would remain for each of the isotopes after 2 days (48 h)?

Solution

This problem is asking us for the percentage of radioactivity remaining after a certain time for both isotopes after 48 hours. We must identify an equation that will help us solve this and we can determine that we can determine this information using the first order equation.

This equation Ln(N/N$_o$)= -kt tells that the Natural log of the fraction remaining is equal to the rate constant times time. To determine the rate constant, we can also compute .693 over the half-life given in the information.

For Technetium-99 we can determine the rate constant by plugging into the second equation: .693/6 hrs= .1155 h^{-1}

Now that we have the rate constant we can plug in : Ln(N/N$_o$)=-(.1155h^{-1})(48h) so Ln(N/N$_o$)=-5.544 and if we take the inverse of the natural log, we get (N/N$_o$)=3.9x10 $^{-3}$ and if we multiply this by 100, we get .39% remaining.

We can do this same process for Thallium-201 and plugin: .693/73 hrs= .009493151 h^{-1} and when we plug this into the first order equation we get:

Ln(N/N$_o$)=-(.009493h^{-1})(48h) so Ln(N/N$_o$)=-.45567248 and when we take the inverse of the natural log, we get (N/N$_o$)=.6340 and when multiplied by 100, we get 63.40% remaining which makes sense since its half-life is 73 hours and only 48 hours have passed, half of the amount has yet to be consumed.

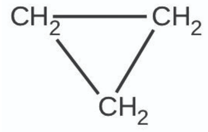
Answer

Technetium-99: 0.39%

Thallium-201: 63.40%

3.E.4.14: Q12.4.14

There are two molecules with the formula C_3H_6. Propene, $\mathrm{CH_3CH{=}CH_2}$, is the monomer of the polymer polypropylene, which is used for indoor-outdoor carpets. Cyclopropane is used as an anesthetic:



When heated to 499 °C, cyclopropane rearranges (isomerizes) and forms propene with a rate constant of $5.95 \times 10^{-4}\ \mathrm{s}^{-1}$. What is the half-life of this reaction? What fraction of the cyclopropane remains after 0.75 h at 499 °C?

Solution

Use the equation

$$t_{1/2} = \frac{ln2}{k}$$

since this is a first-order reaction. You can tell that this is a **first order reaction** due to the units of measurement of the rate constant, which is s^{-1}. Different orders of reactions lead to different rate constants, and a rate constant of s^{-1} will always be first order.

Plug into the equation, and you get half life = 1164.95 seconds. To convert this to hours, we would divide this number by 3600 seconds/hour, to get **0.324 hours**.

Use the integrated first order rate law

$$ln\frac{[A]}{[A]_0} = -kt$$

. In this equation, $[A]_0$ represents the initial amount of compound present at time 0, while [A] represents the amount of compound that is left after the reaction has occurred. Therefore, the fraction

$$\frac{[A]}{[A]_0}$$

is equal to the fraction of cyclopropane that remains after a certain amount of time, in this case, 0.75 hours.

Substitute x for the fraction of

$$\frac{[A]}{[A]_0}$$

into the integrated rate law:

$$ln\frac{[A]}{[A]_0} = -kt$$

$$ln(x) = -5.95x10^{-4}(0.75)$$

$$x = e^{(-0.000595)(0.75)}$$

= 0.20058 = 20%.

So, the half life is 0.324 hours, and 20% of the cyclopropane will remain as 80% will have formed propene.

Answer

0.324 hours. ; 20% remains

3.E.4.15: Q12.4.16

Fluorine-18 is a radioactive isotope that decays by positron emission to form oxygen-18 with a half-life of 109.7 min. (A positron is a particle with the mass of an electron and a single unit of positive charge; the nuclear equation is ${}^{18}_{9}\mathrm{F} \longrightarrow {}^{18}_{8}\mathrm{O} + {}^{0}_{1}\mathrm{e}^{+}$.) Physicians use ^{18}F to study the brain by injecting a quantity of fluoro-substituted glucose into the blood of a patient. The glucose accumulates in the regions where the brain is active and needs nourishment.

a. What is the rate constant for the decomposition of fluorine-18?
b. If a sample of glucose containing radioactive fluorine-18 is injected into the blood, what percent of the radioactivity will remain after 5.59 h?
c. How long does it takFe for 99.99% of the ^{18}F to decay?

Solution

a) The nuclear decay of an isotope of an element is represented by the first order equation:

ln(N/N0) = −kt

Where t is time, N0 is the initial amount of the substance, N is the amount of the substance after time t, and k is the rate constant. We can rearrange the equation and isolate k so that we could solve for the rate constant:

k = [-ln(N/N0)] / t

We are given that fluorine-18 has a half-life of 109.7 minutes. Since we have the half-life, we can choose an arbitrary value for N_0 and use half of that value for N. In this case, we choose 100 for N_0 and 50 for N. Now we can plug in those values into the equation above and solve for k.

k = [-ln(50/100)] / 109.7

k = 0.6931 / 109.7 = 0.006319 min^{-1}

The rate constant for this reaction is 0.006319 min^{-1}.

b) For this problem, we are able to use the same equation from part a:

ln(N/N0) = −kt

However, this time we are given the amount of time elapsed instead of the half-life, and we are asked to determine the percent of fluorine-18 radioactivity remaining after that time. In this problem, we must plug in values for N0, k (determined from part a), and t.

But first, since we are given the elapsed time in hours, we must convert it into minutes:

5.59 hours x (60 minutes / 1 hours) = 335.4 minutes

This gives us the value for t. We also have values for k (0.006319 min^{-1}) and N_0 (again an arbitrary number.) Now we can plug values into the original equation, giving us:

ln(N/100) = −(0.006319)(335.4)

We solve this equation by taking the exponential of both sides:

$$e^{\ln(N/100)} = e^{-(0.006319)(335.4)}$$

where $e^{\ln}$ equals 1 and now we can just solve for N:

$$N/100 = e^{-(0.006319)(335.4)}$$

$$N = [e^{-(0.006319)(335.4)}] \text{ x } 100 = 12.0$$

Since 100 was used as the initial amount and 12.0 was determined as the remaining amount, 12.0 can be used as the percentage of remaining amount of radioactivity of fluorine-18. **Thus the percent of fluorine-18 radioactivity remaining after 5.59 hours is 12.0%.**

c) This part of the question is much like the previous two parts, but this time we are given the initial amount of radioactivity, the final amount of radioactivity and we are asked do determine how long it took for that amount of radioactivity to decay. We are able to use the same equation:

$$\ln(N/N0) = -kt$$

However, now we are given N and N_0 and we have already determined k from before. We are told that 99.99% of the radioactivity has decayed, so we can use 100 and 0.01 for N_0 and N respectively. We plug these values in to the equation, solve for t, and get

$$\ln(0.01/1000) = -0.006319t$$

$$-9.21 = -0.006319t$$

$$t = 1458 \text{ minutes}$$

Therefore, its takes 1458 minutes for 99.99% of the radioactivity to decay.

Answer

a) 0.006319 min^{-1}

b) 12.0%

c) 1458 minutes

3.E.4.16: Q12.4.17

Suppose that the half-life of steroids taken by an athlete is 42 days. Assuming that the steroids biodegrade by a first-order process, how long would it take for $\frac{1}{64}$ of the initial dose to remain in the athlete’s body?

Solution

252 days

for first order reaction: $t_{1/2} = 0.693 / k$

$k = 0.693 / 42$

$k = 0.0165$

for first order reaction: $[A] = [A]_0 e^{-kt}$

1/64 initial means that: $[A] = 1/64 [A]_0$

therefore: $1/64 [A]_0 = [A]_0 e^{-0.0165t}$

$t = 252$ days

3.E.4.17: Q12.4.18

Recently, the skeleton of King Richard III was found under a parking lot in England. If tissue samples from the skeleton contain about 93.79% of the carbon-14 expected in living tissue, what year did King Richard III die? The half-life for carbon-14 is 5730 years.

Solution

In order to find out what year King Richard III died, set $[A]/[A_0]$ (the percent of carbon-14 still contained) equal to $0.5^{\text{time(t)/half life }(t_{1/2})}$ or use the equation $N(t) = N_0e^{-rt.}$

Using the first equation:

$A/A_0 = 0.5^{t/t_{1/2}}$ plug in the given numbers $.9379 = 0.5^{t/5730}$ and solve for t.

$ln.9379 = (t/5730)(ln0.5)$(using the rule of logs)

$-.0641 = (t/5730)(-.693)$

$-367.36 = -.693t$

$t = 530.1 years$

Using $N(t) = N_0e^{-rt}$ this problem is solved by the following:

$1/2 = e^{-5730r}$

$r = 0.000121$

Now that we know what r is, we can use this value in our original formula and solve for t, the amount of years that have passed.

This time, we use 93.78, the percent of the carbon-14 remaining as N(t) and 100 as the original, N_0.

$93.78 = 100e^{-0.000121t}$

$t = 530.7$ years

Another way of doing this is by using these two equations:

$\lambda = \frac{0.693}{t_{1/2}}$ and $\frac{n_t}{n_0} = -\lambda t$

n_t = concentration at time t (93.79)

n_0 = initial concentration (100)

First solve for lambda or the decay constant by plugging in the half life.

Then plug in lambda and the other numbers into the second equation, and solve for t- which should equal to 530.1 years as well.

If we want to find out what year King Richard III died, we take the current year, 2017, and subtract 530 years. Doing this, we find that King Richard III died in the year 1487.

Answer

King Richard III died in the year 1487

3.E.4.18: Q12.4.19

Nitroglycerine is an extremely sensitive explosive. In a series of carefully controlled experiments, samples of the explosive were heated to 160 °C and their first-order decomposition studied. Determine the average rate constants for each experiment using the following data:

Initial $[C_3H_5N_3O_9]$ (*M*)	4.88	3.52	2.29	1.81	5.33	4.05	2.95	1.72
***t* (s)**	300	300	300	300	180	180	180	180
% Decomposed	52.0	52.9	53.2	53.9	34.6	35.9	36.0	35.4

Solution

First we need to understand what the question is asking for: the average rate constant. The average rate constant is the variable "k" when discussing kinetics and it can be defined as the proportionality constant in the equation that expresses the relationship between the rate of a chemical reaction and the concentrations of the reacting substances. Knowing that we need to find K in this first order reaction, we can look to formulas that include "k," initial and final concentrations $[A]_o and [A]_t$, and half life time "t." Since this is a first order reaction, we can look to the first order equations, and doing that we find one that includes the variables given in the question:

$$\ln[A]_t = -kt + \ln[A]_o$$

For the first reaction, we have an initial concentration of 4.88 M, and a percentage decomposed. To find the final concentration, we must multiply the initial concentration by the percentage decomposed to know how much decomposed, and subtract that from the original to find out how much is left: 4.88M x 0.52= 2.54 M and 4.88M-2.54M=2.34M

Now, we have the variables we need, and we plug it into the equation above:

$\ln[A]_t = -kt + \ln[A]_o$

$\ln[2.34M] = -k(300s) + \ln[4.88M]$

k=$\frac{-(\ln[2.34M] - \ln[4.88M])}{300}$

$k = 2.45x10^{-3}$

Since it asks for the rate constant of each experiment, we now must do the same procedure for each data set to find the rate constant:

Second experiment

$\ln[A]_t = -kt + \ln[A]_o$

$\ln[1.66M] = -k(300s) + \ln[3.52M]$

k=$\frac{-(\ln[1.66M] - \ln[3.52M])}{300}$

$k = 2.51x10^{-3}$

Third experiment

$\ln[A]_t = -kt + \ln[A]_o$

$\ln[1.07M] = -k(300s) + \ln[2.29M]$

k=$\frac{-(\ln[1.07M] - \ln[2.29M])}{300}$

$k = 2.54x10^{-3}$

Fourth experiment

$\ln[A]_t = -kt + \ln[A]_o$

$\ln[0.834M] = -k(300s) + \ln[1.81M]$

k=$\frac{-(\ln[0.834M] - \ln[1.81M])}{300}$

$k = 2.58x10^{-3}$

Fifth Experiment

$\ln[A]_t = -kt + \ln[A]_o$

$\ln[3.49M] = -k(180s) + \ln[5.33M]$

k=$\frac{-(\ln[3.49M] - \ln[5.33M])}{180}$

$k = 2.35x10^{-3}$

Sixth Experiment

$\ln[A]_t = -kt + \ln[A]_o$

$\ln[2.60M] = -k(180s) + \ln[4.05M]$

k=$\frac{-(\ln[2.60M]-\ln[4.05M])}{180}$

$k = 2.46x10^{-3}$

Seventh Experiment

$\ln[A]_t = -kt + \ln[A]_o$

$\ln[1.89M] = -k(180s) + \ln[2.95M]$

k=$\frac{-(\ln[1.89M]-\ln[2.95M])}{180}$

$k = 2.47x10^{-3}$

Eighth experiment

$\ln[A]_t = -kt + \ln[A]_o$

$\ln[1.11M] = -k(180s) + \ln[1.72M]$

k=$\frac{-(\ln[1.11M]-\ln[1.72M])}{180}$

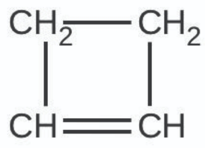
$k = 2.43x10^{-3}$

Answer

$[A]_0$ (*M*)	$k \times 10^3$ (s^{-1})
4.88	2.45
3.52	2.51
2.29	2.54
1.81	2.58
5.33	2.35
4.05	2.44
2.95	2.47
1.72	2.43

3.E.4.19: Q12.4.20

For the past 10 years, the unsaturated hydrocarbon 1,3-butadiene $(CH_2{=}CH{-}CH{=}CH_2)$ has ranked 38th among the top 50 industrial chemicals. It is used primarily for the manufacture of synthetic rubber. An isomer exists also as cyclobutene:



The isomerization of cyclobutene to butadiene is first-order and the rate constant has been measured as 2.0 × 10^{-4} s^{-1} at 150 °C in a 0.53-L flask. Determine the partial pressure of cyclobutene and its concentration after 30.0 minutes if an isomerization reaction is carried out at 150 °C with an initial pressure of 55 torr.

Solution

Since this is a first order reaction, the integrated rate law is: $[A_t] = [A_0]e^{-kt}$
Partial Pressure: Use the integrated rate law to find the partial pressure at 30 minutes:

Use A_0 = 55 torr, t = 30 min, and k = $2.0 * 10^{-4} s^{-1}$ to solve the integrated rate law equation:

$[A_{30}] = (55torr) * e^{-(2.0x10^{-4}\frac{1}{sec})(30min\cdot\frac{60sec}{1min})}$

Solve this equation to get:

$[A_{30}] = (55torr) * e^{-0.36}$

$A_{30}]$ = 38.37 torr.

Initial Concentration: Find the initial concentration using the ideal gas law.

The ideal gas law is given by $PV = nRT \rightarrow n = \frac{PV}{RT}$. Use this form of the gas law to solve for the initial concentration n.

Use V = 0.53L, R = 0.08206 $\frac{L*atm}{mol*L}$, T = 423.15 K, and P = $\frac{1atm}{760}$ = 0.07237 atm .

Solve the ideal gas equation using these values:

$$n = \frac{(55torr)(0.53L)}{(0.08206\frac{L*atm}{mol*K})(423.15K)} = 0.00110 \text{ moles cyclobutene.}$$

Now find the initial concentration of cyclobutene A_0 using the equation $[A_0] = \frac{n}{V}$:

$$A_0 = \frac{n}{V} = \frac{0.00110moles}{0.53L} = 0.00208M$$

Concentration at 30 minutes: Find the concentration of cyclobutene at 30 minutes by using the integrated rate law given above, using time t = 30 minutes, or 1800 seconds.

$$[A_{30}] = (0.00208M)e^{-0.36} = 0.00145M$$

So at 30 minutes, the cyclobutene concentration is 0.00145 M, and the partial pressure is 38.37 torr.

Answer

Partial Pressure: 38.37 torr.

Concentration: 0.00145 M

3.E.5: 12.5: Collision Theory

3.E.5.1: Q12.5.1

Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

Solution

The two factors that may prevent a collision from producing a chemical reaction are:

1. **Kinetic energy of the molecule**

In order for chemical reactions to occur, molecules require enough velocity to overcome the minimum activation energy needed to break the old bonds and form new bonds with other molecules. At higher temperatures, the molecules possess the minimum amount of kinetic energy needed which ensures the collisions will be energetic enough to lead to a reaction.

2. **The orientation of molecules during the collision**

Two molecules have to collide in the right orientation in order for the reaction to occur. Molecules have to orient properly for another molecule to collide at the right activation state.

3.E.5.2: Q12.5.2

When every collision between reactants leads to a reaction, what determines the rate at which the reaction occurs?

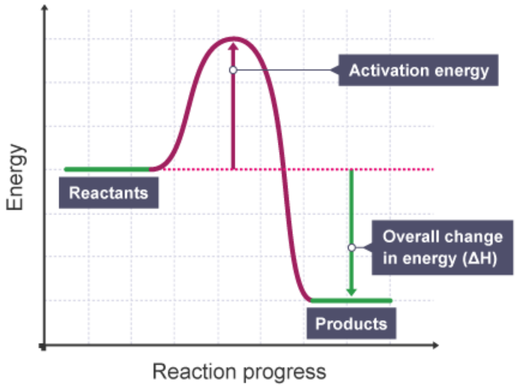
Solution

There has to be contact between reactants for a reaction to occur. The more the reactants collide, the more often reactions can occur. Factors that determine reaction rates include concentration of reactants, temperature, physical states of reactants, surface area, and the use of a catalyst. The reaction rate usually increases as the concentration of a reactant increases. Increasing the temperature increases the average kinetic energy of molecules, causing them to collide more frequently, which increases the reaction rate. When two reactants are in the same fluid phase, their particles collide more frequently, which increases the reaction rate. If the surface area of a reactant is increased, more particles are exposed to the other reactant therefore more collisions occur and the rate of reaction increases. A catalyst participates in a chemical reaction and increases the reaction rate without changing itself.

3.E.5.3: Q12.5.3

What is the activation energy of a reaction, and how is this energy related to the activated complex of the reaction?

Solution



Activation energy is the energy barrier that must be overcome in order for a reaction to occur. To get the molecules into a state that allows them to break and form bonds, the molecules must be contorted (deformed, or bent) into an unstable state called the transition state. The transition state is a high-energy state, and some amount of energy – the activation energy – must be added in order for the molecule reach it. Because the transition state is unstable, reactant molecules don’t stay there long, but quickly proceed to the next step of the chemical reaction.The activated complex is the highest energy of the transition state of the reaction.

3.E.5.4: Q12.5.5

Describe how graphical methods can be used to determine the activation energy of a reaction from a series of data that includes the rate of reaction at varying temperatures.

Solution

This method is based on the **Arrhenius equation** which can be used to show the effect of a change of temperature on the **rate constant**, and therefore on the rate of reaction.

The rate constant is different from reaction rat in that the reaction rate is the measure of how fast or slow a chemical reaction takes place while a rate constant is a constant that shows the relationship between the reaction rate and the concentrations of the reactants or products.

For example, for the reaction $A + B \rightarrow C$, the rate law would be:

$$rate = k[A]^a[B]^b$$

k = rate constant

[A] = concentration of reactant A

a = order of reaction with respect to A

[B] = concentration of reactant B

b = order of reaction with respect to B

However, the rate constant remains constant only if you are changing the concentration of the reactants. If you change the temperature or the catalyst of the reaction, the rate constant will change and this is demonstrated by the Arrhenius equation:

$$k = Ae^{\frac{-E_a}{RT}}$$

$$ln\left(\frac{k_1}{k_2}\right)=\left(\frac{-E_a}{R}\right)\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

k = rate constant

A = frequency factor

E_a = activation energy

e = exponential function, e^x

R = gas constant

T = temperature (K)

In other words, the activation energy of a reaction, E_a, from a series of data that includes the rate of reaction, k, at varying temperatures can be determined by graphing it on a plot of $\ln k$ versus $\frac{1}{T}$. You can then use the slope of the graph you have plotted to solve for E_a by setting the slope equal to $\frac{-E_a}{R}$.

3.E.5.5: Q12.5.6

How does an increase in temperature affect rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.

3.E.5.6: S12.5.6

Collision theory states that the rates of chemical reactions depend on the fraction of molecules with the correct orientation, fraction of collisions with required energy, and the collision frequency. Because the fraction of collisions with required energy is a function of temperature, as temperature increases, the fraction of collisions with required energy also increases. The kinetic energy of reactants also increases with temperature which means molecules will collide more often increasing collisions frequency. With increased fraction of collisions with required energy and collisions frequency, the rate of chemical reaction increases. We see mathematically, from the Arrhenius equation, that temperature and the rate constant are related.

$$k=Ae^{\frac{E_a}{RT}} \tag{3.E.14}$$

where k is the rate constant, A is a specific constant, R is 8.3145 J/K, Ea is the reaction-specific activation energy in J, and T is temperature in K. We see from the equation that k is very sensitive to changes in the temperature.

3.E.5.7: Q12.5.7

The rate of a certain reaction doubles for every 10 °C rise in temperature.

a. How much faster does the reaction proceed at 45 °C than at 25 °C?
b. How much faster does the reaction proceed at 95 °C than at 25 °C?

Solution

By finding the difference in temperature, 45 °C - 25 °C, we get 20 °C. Since the rate of the reaction doubles every 10 °C increase in temperature and the rate of the reaction experienced a 20 °C increase in temperature, we see that the reaction rate doubled twice (2^2 = 4). As a result, the **reaction proceeds four times faster**.

Following the same process as in part a, we get the difference in temperature to be 70 °C. Since the rate of the reaction doubles every 10 °C increase in temperature and the system experienced a 70 °C change, we see that the reaction doubled seven times (2^7 = 128). We can see the **reaction proceeds 128 times faster**.

(a) 4-times faster (b) 128-times faster

3.E.5.8: Q12.5.8

In an experiment, a sample of $NaClO_3$ was 90% decomposed in 48 min. Approximately how long would this decomposition have taken if the sample had been heated 20 °C higher?

3.E.5.9: S12.5.8

First off, it is important to recognize that this decomposition reaction is a **first-order reaction**, which can be written as follows: $2NaClO_3 \rightarrow 2NaCl + 3O_2$

Understanding this, it is important to be able to then be able to recognize which equation would be most useful given the initial conditions presented by the question. Since we are dealing with time, percentage of material left, and temperature, the only viable equation that could relate all of this would be the Arrhenius Equation, which is written as follows: $\ln(\frac{k_2}{k_1}) = \frac{Ea}{R}(\frac{1}{t_1} - \frac{1}{t_2})$

However, this problem does not give us enough information such as what the activation energy is or the initial temperature in order to mathematically solve this problem. Additionally, the problem tells us to approximate how long the decomposition would take, which means we are asked to answer this question conceptually based on our knowledge of thermodynamics and reaction rates. As a general rule of thumb, we know that for every 10˚C rise in temperature the rate of reaction doubles. Since the question tells us that there is a 20˚C rise in temperature we can deduce that the reaction rate doubles twice, as per the general rule mentioned before. This means **the overall reaction rate for this decomposition would quadruple**, or would be 4 times faster than the reaction rate at the initial temperature.

We can gut check this answer by recalling how an increase in the average kinetic energy (temperature) decreases the time it takes for the reaction to take place and increase the reaction rate. Thus, if we increase the temperature we should have a faster reaction rate.

3.E.5.10: Q12.5.9

The rate constant at 325 °C for the decomposition reaction $\mathrm{C_4H_8 \longrightarrow 2\,C_2H_4}$ is $6.1 \times 10^{-8}\ \mathrm{s^{-1}}$, and the activation energy is 261 kJ per mole of C_4H_8. Determine the frequency factor for the reaction.

Solution

3.E.5.11: S12.5.9

Using the Arrhenius equation allows me to find the frequency factor, A.

$k=Ae^{-Ea/RT}$

k, Ea, R, and T are all known values. k, Ea, and T are given in the problem as 6.1×10^{-8}, 261 kJ, and 598 K, respectively.

So, plugging them into the equation gives:

$6.1 \times 10^{-8}\ s^{-1} = Ae^{(-261000\ J)/(8.3145\ J/mol)(598\ K)}$

Take $e^{(-261000\ J)/(8.3145\ J/mol)(598)}$ and get 1.59×10^{-23}. Divide k, 6.1×10^{-8}, by 1.59×10^{-23} and get $A = 3.9 \times 10^{15} s^{-1}$

3.E.5.12: A12.5.9

$3.9 \times 10^{15}\ \mathrm{s^{-1}}$

3.E.5.13: Q12.5.10

The rate constant for the decomposition of acetaldehyde (CH_3CHO), to methane (CH_4), and carbon monoxide (CO), in the gas phase is 1.1×10^{-2} L/mol/s at 703 K and 4.95 L/mol/s at 865 K. Determine the activation energy for this decomposition.

3.E.5.14: S12.5.10

The equation for relating the rate constant and activation energy of a reaction is the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \tag{3.E.15}$$

When given two rate constants at two different temperatures but for the same reaction, the Arrhenius equation can be rewritten as:

$$ln(\frac{k_2}{k_1}) = \frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2}) \tag{3.E.16}$$

In this problem, all the variables are given except for the E_a (activation energy).

$k_1 = 1.1 \times 10^{-2}$ L/mol/s

$T_1 = 703$ K

k_2 = 4.95 L/mol/s

T_2 = 865 K

R = 8.314 J/(mol K) (Ideal Gas Constant)

Now plug in all these values into the equation, and solve for E_a.

$$ln(\frac{4.95\frac{L}{mol\times s}}{1.1\times10^{-2}\frac{L}{mol\times s}})=\frac{E_a}{8.314\times10^{-3}\frac{kJ}{mol\times K}}(\frac{1}{703}-\frac{1}{865}) \tag{3.E.17}$$

E_a = 190 kJ (2 sig figs)

3.E.5.15: Q12.5.11

An elevated level of the enzyme alkaline phosphatase (ALP) in the serum is an indication of possible liver or bone disorder. The level of serum ALP is so low that it is very difficult to measure directly. However, ALP catalyzes a number of reactions, and its relative concentration can be determined by measuring the rate of one of these reactions under controlled conditions. One such reaction is the conversion of p-nitrophenyl phosphate (PNPP) to p-nitrophenoxide ion (PNP) and phosphate ion. Control of temperature during the test is very important; the rate of the reaction increases 1.47 times if the temperature changes from 30 °C to 37 °C. What is the activation energy for the ALP–catalyzed conversion of PNPP to PNP and phosphate?

Solution

43.0 kJ/mol

3.E.5.16: Q12.5.12

In terms of collision theory, to which of the following is the rate of a chemical reaction proportional?

a. the change in free energy per second
b. the change in temperature per second
c. the number of collisions per second
d. the number of product molecules

3.E.5.17: Q12.5.13

Hydrogen iodide, HI, decomposes in the gas phase to produce hydrogen, H_2, and iodine, I_2. The value of the rate constant, *k*, for the reaction was measured at several different temperatures and the data are shown here:

Temperature (K)	k (M^{-1} s^{-1})
555	6.23×10^{-7}
575	2.42×10^{-6}
645	1.44×10^{-4}
700	2.01×10^{-3}

What is the value of the activation energy (in kJ/mol) for this reaction?

Solution

177 kJ/mol

3.E.5.18: Q12.5.14

The element Co exists in two oxidation states, Co(II) and Co(III), and the ions form many complexes. The rate at which one of the complexes of Co(III) was reduced by Fe(II) in water was measured. Determine the activation energy of the reaction from the following data:

T (K)	k (s^{-1})

T (K)	*k* (s^{-1})
293	0.054
298	0.100

3.E.5.19: Q12.5.15

The hydrolysis of the sugar sucrose to the sugars glucose and fructose,

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

follows a first-order rate equation for the disappearance of sucrose: Rate = $k[C_{12}H_{22}O_{11}]$ (The products of the reaction, glucose and fructose, have the same molecular formulas but differ in the arrangement of the atoms in their molecules.)

a. In neutral solution, $k = 2.1 \times 10^{-11}\ s^{-1}$ at 27 °C and $8.5 \times 10^{-11}\ s^{-1}$ at 37 °C. Determine the activation energy, the frequency factor, and the rate constant for this equation at 47 °C (assuming the kinetics remain consistent with the Arrhenius equation at this temperature).
b. When a solution of sucrose with an initial concentration of 0.150 *M* reaches equilibrium, the concentration of sucrose is 1.65×10^{-7} *M*. How long will it take the solution to reach equilibrium at 27 °C in the absence of a catalyst? Because the concentration of sucrose at equilibrium is so low, assume that the reaction is irreversible.
c. Why does assuming that the reaction is irreversible simplify the calculation in part (b)?

Solution

E_a = 108 kJ

$A = 2.0 \times 10^{8}\ s^{-1}$

$k = 3.2 \times 10^{-10}\ s^{-1}$

(b) 1.81×10^{8} h or 7.6×10^{6} day. (c) Assuming that the reaction is irreversible simplifies the calculation because we do not have to account for any reactant that, having been converted to product, returns to the original state.

3.E.5.20: Q12.5.16

Use the PhET Reactions & Rates interactive simulation to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “straight shot” default option, try launching the *A* atom with varying amounts of energy. What changes when the Total Energy line at launch is below the transition state of the Potential Energy line? Why? What happens when it is above the transition state? Why?

3.E.5.21: Q12.5.17

Use the PhET Reactions & Rates interactive simulation to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “angled shot” option, try launching the *A* atom with varying angles, but with more Total energy than the transition state. What happens when the *A* atom hits the *BC* molecule from different directions? Why?

Solution

The *A* atom has enough energy to react with *BC*; however, the different angles at which it bounces off of *BC* without reacting indicate that the orientation of the molecule is an important part of the reaction kinetics and determines whether a reaction will occur.

3.E.6: 12.6: Reaction Mechanisms

3.E.6.1: Q12.6.1

Why are elementary reactions involving three or more reactants very uncommon?

3.E.6.2: Q12.6.2

In general, can we predict the effect of doubling the concentration of *A* on the rate of the overall reaction $A+B \longrightarrow C$? Can we predict the effect if the reaction is known to be an elementary reaction?

Solution

Add texts here. Do not delete this text first.

No. In general, for the overall reaction, we cannot predict the effect of changing the concentration without knowing the rate equation. Yes. If the reaction is an elementary reaction, then doubling the concentration of *A* doubles the rate.

3.E.6.3: Q12.6.3

Phosgene, $COCl_2$, one of the poison gases used during World War I, is formed from chlorine and carbon monoxide. The mechanism is thought to proceed by:

step 1:	$Cl + CO \rightarrow COCl$
step 2:	$COCl + Cl_2 \rightarrow COCl_2 + Cl$

a. Write the overall reaction equation.
b. Identify any reaction intermediates.
c. Identify any intermediates.

3.E.6.4: Q12.6.4

Define these terms:

a. unimolecular reaction
b. bimolecular reaction
c. elementary reaction
d. overall reaction

3.E.6.5: Q12.6.5

What is the rate equation for the elementary termolecular reaction $A+2B \longrightarrow \text{products}$? For $3A \longrightarrow \text{products}$?

Solution

Add texts here. Do not delete this text first.

We are given that both of these reactions are elementary termolecular. The molecularity of a reaction refers to the number of reactant particles that react together with the proper and energy and orientation. Termolecular reactions have three atoms to collide simultaneously. As it is termolecular, and there are no additional reactants aside from the three given in each reaction, there are no intermediate reactions. The rate law for elementary reactions is determined by the stoichiometry of the reaction without needed experimental data.

The basic rate form for the elementary step is what follows:

$rate = k \cdot reactant\ 1^{i} \cdot reactant\ 2^{ii} \cdot \ldots$ Where i and ii are the stochiometric coefficient from reactant 1 and 2 respectively.

For: $3A \rightarrow products$

$k \cdot A^3 = rate$

For: $A+2B \rightarrow products$

$k \cdot [A] \cdot [B]^2 = rate$

Note that the order of these reactions are both three.

Answer

Add texts here. Do not delete this text first.

Rate = $k[A][B]^2$; Rate = $k[A]^3$

3.E.6.6: Q12.6.6

Given the following reactions and the corresponding rate laws, in which of the reactions might the elementary reaction and the overall reaction be the same?

(a) $\mathrm{Cl_2 + CO \longrightarrow Cl_2CO}$

$\mathrm{rate} = k[\mathrm{Cl_2}]^{\frac{3}{2}}[\mathrm{CO}]$

(b) $\mathrm{PCl_3 + Cl_2 \longrightarrow PCl_5}$

$\mathrm{rate} = k[\mathrm{PCl_3}][\mathrm{Cl_2}]$

(c) $\mathrm{2\,NO + H_2 \longrightarrow N_2 + H_2O}$

$\mathrm{rate} = k[\mathrm{NO}][\mathrm{H_2}]$

(d) $\mathrm{2\,NO + O_2 \longrightarrow 2\,NO_2}$

$\mathrm{rate} = k[\mathrm{NO}]^2[\mathrm{O_2}]$

(e) $\mathrm{NO + O_3 \longrightarrow NO_2 + O_2}$

$\mathrm{rate} = k[\mathrm{NO}][\mathrm{O_3}]$

Solution

Add texts here. Do not delete this text first.

An elementary reaction is a chemical reaction in which the reactants directly form products in a single step. In another words, the rate law for the overall reaction is same as experimentally found rate law. Out of 5 options, option (b),(d), and (e) are such reactions

3.E.6.7: Q12.6.7

Write the rate equation for each of the following elementary reactions:

a. $\mathrm{O_3 \xrightarrow{sunlight} O_2 + O}$
b. $\mathrm{O_3 + Cl \longrightarrow O_2 + ClO}$
c. $\mathrm{ClO + O \longrightarrow Cl + O_2}$
d. $\mathrm{O_3 + NO \longrightarrow NO_2 + O_2}$
e. $\mathrm{NO_2 + O \longrightarrow NO + O_2}$

Solution

Add texts here. Do not delete this text first.

Rate equations are **dependent on the reactants and not the products.**

The rate law of a reaction can be found using a rate constant (which is found experimentally), and the initial concentrations of reactants.

A general solution for the equation

$aA + bB \rightarrow cC + dD$

is $rate = k[A]^m[B]^n$ where m and n are reaction orders.

However, reaction orders are found experimentally, and since we do not have experimental data for these reactions, we can disregard that part of the equation.

To find the rate laws, all we have to do is plug the reactants into the rate formula. This is only due to the case that these are elementary reactions. Further reading on elementary reactions can be found on Libre Texts.

a. $\mathrm{O_3 \longrightarrow O_2 + O}$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[O_3]$$

b. $O_3 + Cl \longrightarrow O_2 + ClO$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[O_3][Cl]$$

c. $ClO + O \longrightarrow Cl + O_2$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[ClO][O]$$

d. $O_3 + NO \longrightarrow NO_2 + O_2$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[O_3][NO]$$

e. $NO_2 + O \longrightarrow NO + O_2$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[NO_2][O]$$

Answer

Add texts here. Do not delete this text first.

(a) $\text{Rate}_1 = k[O_3]$; (b) $\text{Rate}_2 = k[O_3][Cl]$; (c) $\text{Rate}_3 = k[ClO][O]$; (d) $\text{Rate}_2 = k[O_3][NO]$; (e) $\text{Rate}_3 = k[NO_2][O]$

3.E.6.8: Q12.6.8

Nitrogen(II) oxide, NO, reacts with hydrogen, H_2, according to the following equation:

$$2\,NO + 2\,H_2 \longrightarrow N_2 + 2\,H_2O$$

What would the rate law be if the mechanism for this reaction were:

$$2\,NO + H_2 \longrightarrow N_2 + H_2O_2 \text{ (slow)}$$

$$H_2O_2 + H_2 \longrightarrow 2\,H_2O \text{ (fast)}$$

The rate law of the mechanism is determined by the slow step of the reaction. Since the slow step is an elementary step, the rate law can be drawn from the coefficients of the chemical equation. So therefore, the rate law is as follows: rate=$k[NO]^2[H_2]$. Since both NO and H_2 are reactants in the overall reaction (therefore are not intermediates in the reaction), no further steps have to be done to determine the rate law.

3.E.6.9: Q12.6.9

Consider the reaction

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ (occurs under light)

The mechanism is a chain reaction involving Cl atoms and CH_3 radicals. Which of the following steps does not terminate this chain reaction?

a. $CH_3 + Cl \rightarrow CH_3CI$
b. $CH_3 + HCl \rightarrow CH_4 + Cl$
c. $CH_3 + CH_3 \rightarrow C_2H_2$

d. Cl + Cl → Cl_2

Solution

Add texts here. Do not delete this text first.

Chain reactions involve reactions that create products necessary for more reactions to occur. In this case, a reaction step will continue the chain reaction if a radical is generated. Radicals are highly reactive particles, so more reactions in the chain will take place as long as they are present. The chlorine is considered a free radical as it has an unpaired electron; for this reason it is very reactive and propagates a chain reaction. It does so by taking an electron from a stable molecule and making that molecule reactive, and that molecule goes on to react with stable species, and in that manner a long series of "chain" reactions are initiated. A chlorine radical will continue the chain by completing the following reaction:

$$Cl\cdot + CH_4 \rightarrow CH_3\cdot + HCl$$

The CH_3 generated by this reaction can then react with other species, continuing to propagate the chain reaction.

Option 1 is incorrect because the only species it produces is CH_3Cl, a product in the overall reaction that is unreactive. This terminates the chain reaction because it fails to produce any Cl or CH_3 radicals that are necessary for further propagating the overall reaction.

Option 2 is the correct answer because it produces a Cl radical. This Cl radical can continue the chain by colliding with CH_4 molecules.

Option 3 is incorrect because it fails to produce a radical capable of continuing the chain.

Option 4 is incorrect because it produces Cl_2, a molecule that does not react unless additional light is supplied. Therefore, this step breaks the chain.

Answer

Add texts here. Do not delete this text first.

Answer: Option 2: $CH_3 + HCl \rightarrow CH_4 + Cl$

3.E.6.10: Q12.6.10

Experiments were conducted to study the rate of the reaction represented by this equation.

$$2\,\mathrm{NO}(g) + 2\,\mathrm{H_2}(g) \longrightarrow \mathrm{N_2}(g) + 2\,\mathrm{H_2O}(g)$$

Initial concentrations and rates of reaction are given here.

Experiment	Initial Concentration [NO] (mol/L)	Initial Concentration, [H_2] (mol/L)	Initial Rate of Formation of N_2 (mol/L min)
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

Consider the following questions:

a. Determine the order for each of the reactants, NO and H_2, from the data given and show your reasoning.
b. Write the overall rate law for the reaction.
c. Calculate the value of the rate constant, *k*, for the reaction. Include units.
d. For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 had been consumed.
e. The following sequence of elementary steps is a proposed mechanism for the reaction.

Step 1: $\mathrm{NO} + \mathrm{NO} \rightleftharpoons \mathrm{N_2O_2}$

Step 2: $N_2O_2 + H_2 \rightleftharpoons H_2O + N_2O$

Step 3: $N_2O + H_2 \rightleftharpoons N_2 + H_2O$

Based on the data presented, which of these is the rate determining step? Show that the mechanism is consistent with the observed rate law for the reaction and the overall stoichiometry of the reaction.

S12.6.10

1. i) Find the order for [NO] by using experiment 3 and 4 where [H_2] is constant

Notice that [NO] doubles from experiment 3 to 4 and the rate quadruples. So the order for [NO] is **2**

ii) Find the order for [H_2] by using experiment 1 and 2 where [NO] is constant

Notice that [H_2] doubles from experiment 1 to 2 and the rate doubles as well. So the order for [H_2] is **1**

2. Put in the order for each product as the exponents for the corresponding reactant.

$$rate = k[NO]^2[H_2]$$

3. Put in the concentrations and the rate from one of the experiments into the rate law and solve for k. (Here, experiement 1 is used but any of them will work)

$$rate = k[NO]^2[H_2] \;\; .00018 = k[.006]^2[.001] k = 5000 M^{-2} s^{-1}$$

4. Plug in values for experiment 2 into the rate law equation and solve for the concentration of NO

$$.00036 = 5000[NO]^2[.001] [NO]^2 = 7.2x10^{-5} \;\; [NO] = .0085M$$

5. Write the rate laws for each step and then see which matches the rate law we found in question 2. The rate determining step (the slow step) is the one that gives the rate for the overall reaction. Because of this, only those concentrations will influence the overall reaction, contrary to what we would believe if we just looked at the overall reaction.

Step 1: $NO + NO \rightleftharpoons N_2O_2$

$rate = k_1[NO]^2$ This rate law is not the same as the one we calculate in question 2 so this **can not** be the rate determining step

Step 2: $N_2O_2 + H_2 \rightleftharpoons N_2O + N_2O$

$rate = k_2[N_2O_2][H_2]$

Since N_2O_2 is an intermediate you must replace it in the rate law equation. Intermediates can not be in the rate law because they do not appear in the overall reaction. Here you can take the reverse of equation 1 (k_{-1}) and substitute the other side (the reactants of equation 1) for the intermediate in the rate law equation.

$$rate_1 = rate_{-1}$$

$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

$$[N_2O_2] = \frac{k_1[NO]^2}{k_{-1}}$$

$rate = \frac{k_2 k_1 [NO]^2 [H_2]}{k_{-1}}$

Overall: $rate = k[NO]^2[H_2]$ This **is the same** so it is the rate determining step.

So $N_2O_2 + H_2 \rightleftharpoons N_2O + N_2O$ is the rate determining step step.

Answer

Add texts here. Do not delete this text first.

(a) NO: 2

H_2 : 1

(b) Rate = k [NO]^2[H_2];

(c) $k = 5.0 \times 10^3\ \text{mol}^{-2}\ \text{L}^{-2}\ \text{min}^{-1}$;

(d) 0.0050 mol/L;

(e) Step II is the rate-determining step.

3.E.6.11: Q12.6.11

The reaction of CO with Cl_2 gives phosgene ($COCl_2$), a nerve gas that was used in World War I. Use the mechanism shown here to complete the following exercises:

- $\mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{Cl}(g)$ (fast, k_1 represents the forward rate constant, k_{-1} the reverse rate constant)
- $\mathrm{CO}(g) + \mathrm{Cl}(g) \longrightarrow \mathrm{COCl}(g)$ (slow, k_2 the rate constant)
- $\mathrm{COCl}(g) + \mathrm{Cl}(g) \longrightarrow \mathrm{COCl_2}(g)$ (fast, k_3 the rate constant)

a. Write the overall reaction.
b. Identify all intermediates.
c. Write the rate law for each elementary reaction.
d. Write the overall rate law expression.

Solution

Add texts here. Do not delete this text first.

1. To write the overall reaction you have to identify the intermediates and leave them out. The easiest way to do this is to write out all the products and reactants and cross out anything that is on both sides.

Cl_2(g) + CO(g) + ~~2Cl(g)~~ +~~COCl(g)~~ ⇒ ~~2Cl(g)~~ + ~~COCl(g)~~ + $COCl_2$(g)

In this you will cross out the 2Cl(g) molecules and the COCl(g). What is left after that is the overall reaction.

Cl_2(g) + CO(g) ⇒ + $COCl_2$(g)

2. For part two you will just list the intermediates that you crossed out.

Cl and COCl are intermediates

3. Each rate law will be the rate equal to the rate constant times the concentrations of the reactants

reaction 1

(forward) rate=$k_1[Cl_2]$ (reverse) rate=$k_{-1}[Cl]$

reaction 2

rate=$k_2[CO][Cl]$

Reaction 3

rate=$k_3[COCl][Cl]$

4. The overall rate law is based off the slowest step (step #2), since it is the rate determining step, but Cl is present in that rate law so we have to replace it with an equivalent that does not contain an intermediate. To do this you use the equilibrium since the rates are the same you can set up the rate laws of the forward and reverse equal to each other.

$k_1[Cl_2] = k_{-1}[Cl]$

$[Cl]= k_1[Cl_2]/k_{-1}$

rate=$k_2[CO]k_1[Cl_2]/k_{-1}$

rate=$k^\circ[CO][Cl_2]$

Steps to replacing and intermediate

1. Set the forward and reverse reaction equal to each other using separate constants
2. Solve for the intermediate using algebra
3. Plug into the rate determining formula

4. All the k's will be condensed into a K prime constant

3.E.7: 12.7: Catalysis

3.E.7.1: Q12.7.1

Account for the increase in reaction rate brought about by a catalyst.

3.E.7.2: Q12.7.2

Compare the functions of homogeneous and heterogeneous catalysts.

3.E.7.3: Q12.7.3

Consider this scenario and answer the following questions: Chlorine atoms resulting from decomposition of chlorofluoromethanes, such as CCl_2F_2, catalyze the decomposition of ozone in the atmosphere. One simplified mechanism for the decomposition is:

$$\begin{gathered} O_3 \xrightarrow{\text{sunlight}} O_2 + O \\ O_3 + Cl \longrightarrow O_2 + ClO \\ ClO + O \longrightarrow Cl + O_2 \end{gathered}$$

a. Explain why chlorine atoms are catalysts in the gas-phase transformation:

$$2\,O_3 \longrightarrow 3\,O_2$$

b. Nitric oxide is also involved in the decomposition of ozone by the mechanism:

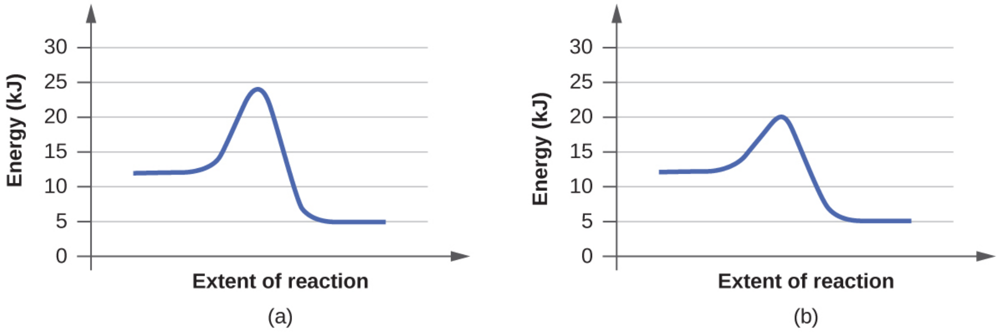
$$\begin{gathered} O_3 \xrightarrow{\text{sunlight}} O_2 + O \\ O_3 + NO \longrightarrow NO_2 + O_2 \\ NO_2 + O \longrightarrow NO + O_2 \end{gathered}$$

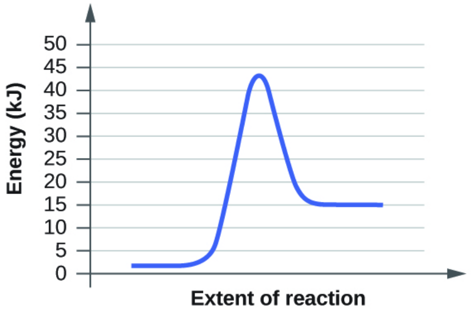
Is NO a catalyst for the decomposition? Explain your answer.

3.E.7.4: Q12.7.4

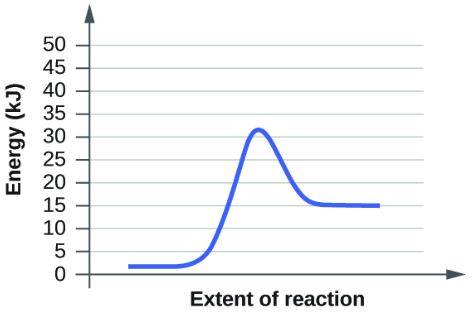
For each of the following pairs of reaction diagrams, identify which of the pair is catalyzed:

(a)





(a)

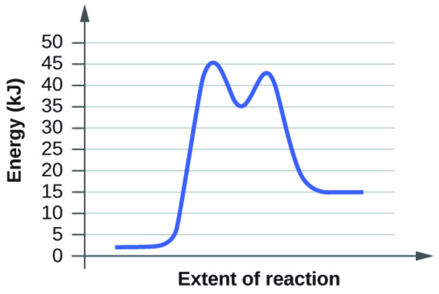


(b)

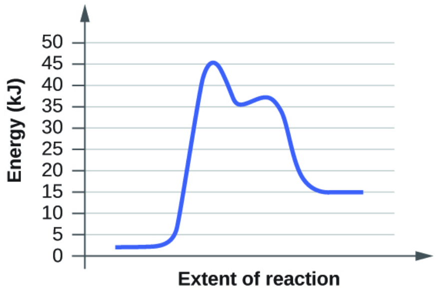
3.E.7.5: Q12.7.5

For each of the following pairs of reaction diagrams, identify which of the pairs is catalyzed:

(a)

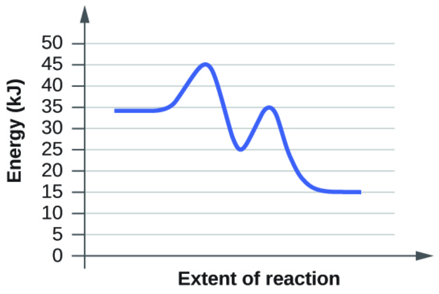


(a)

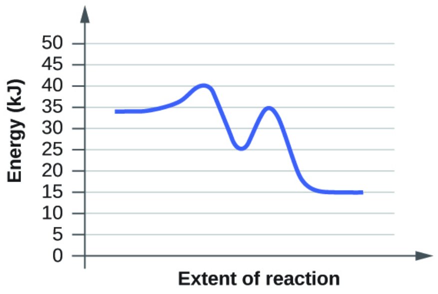


(b)

(b)



(a)

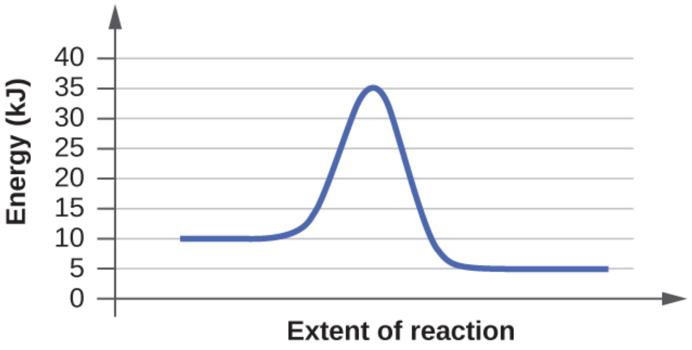


(b)

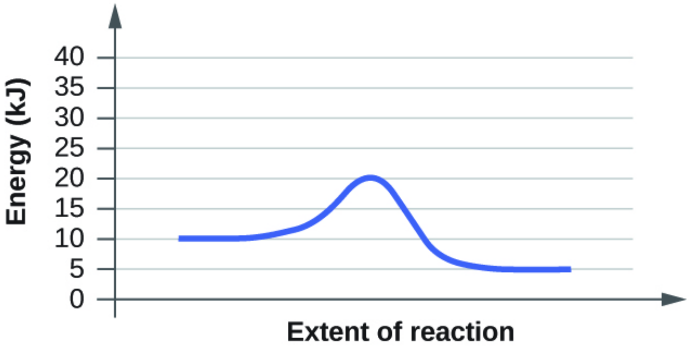
3.E.7.6: Q12.7.6

For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



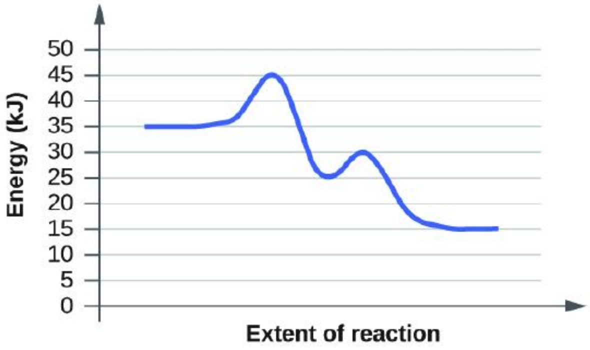
(b)



3.E.7.7: Q12.7.7

For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



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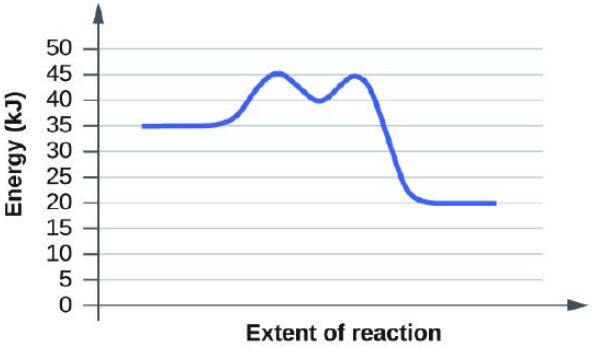

3.E.7.8: Q12.7.8

1. Based on the diagrams in Question Q12.7.6, which of the reactions has the fastest rate? Which has the slowest rate?
2. Based on the diagrams in Question Q12.7.7, which of the reactions has the fastest rate? Which has the slowest rate?

CHAPTER OVERVIEW

4: Chemical Equilibrium

4.1: Chemical Equilibria

Learning Objectives

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

A chemical reaction is usually written in a way that suggests it proceeds in one direction, the direction in which we read, but all chemical reactions are reversible, and both the forward and reverse reaction occur to one degree or another depending on conditions. In a chemical equilibrium, the forward and reverse reactions occur at equal rates, and the concentrations of products and reactants remain constant. If we run a reaction in a closed system so that the products cannot escape, we often find the reaction does not give a 100% yield of products. Instead, some reactants remain after the concentrations stop changing. At this point, when there is no further change in concentrations of reactants and products, we say the reaction is at equilibrium. A mixture of reactants and products is found at equilibrium.

For example, when we place a sample of dinitrogen tetroxide (N_2O_4, a colorless gas) in a glass tube, it forms nitrogen dioxide ($\mathrm{NO_2}$, a brown gas) by the reaction

$$\mathrm{N_2O_4(g) \rightleftharpoons 2\,NO_2(g)} \tag{4.1.1}$$

The color becomes darker as $\mathrm{N_2O_4}$ is converted to $\mathrm{NO_2}$. When the system reaches equilibrium, both $\mathrm{N_2O_4}$ and $\mathrm{NO_2}$ are present (Figure 4.1.1).

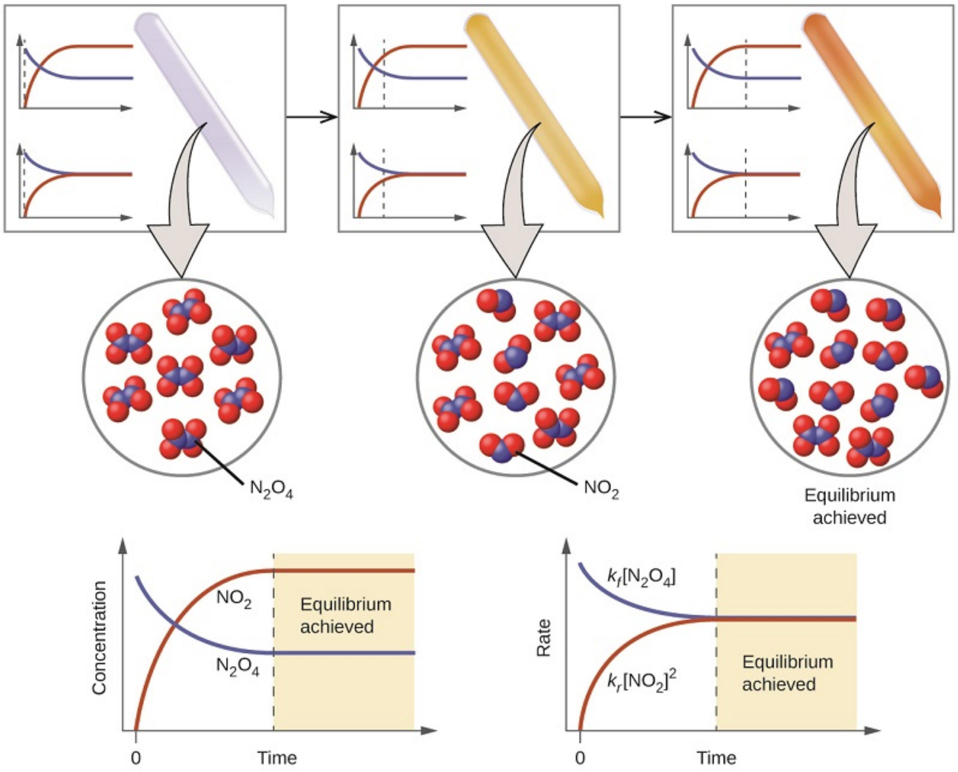

Figure 4.1.1: A mixture of $\mathrm{NO_2}$ and $\mathrm{N_2O_4}$ moves toward equilibrium. Colorless $\mathrm{N_2O_4}$ reacts to form brown $\mathrm{NO_2}$. As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of $\mathrm{NO_2}$.

The formation of $\mathrm{NO_2}$ from $\mathrm{N_2O_4}$ is a reversible reaction, which is identified by the equilibrium arrow ($\rightleftharpoons$). All reactions are reversible, but many reactions, for all practical purposes, proceed in one direction until the reactants are exhausted and will reverse only under certain conditions. Such reactions are often depicted with a one-way arrow from reactants to products. Many other reactions, such as the formation of $\mathrm{NO_2}$ from $\mathrm{N_2O_4}$, are reversible under more easily obtainable conditions and, therefore, are named as such. In a reversible reaction, the reactants can combine to form products and the products can react to form the reactants. Thus, not only can $\mathrm{N_2O_4}$ decompose to form $\mathrm{NO_2}$, but the $\mathrm{NO_2}$ produced can react to form $\mathrm{N_2O_4}$. As soon as the forward reaction produces any NO_2, the reverse reaction begins and NO_2 starts to react to form N_2O_4. At equilibrium, the concentrations of N_2O_4 and NO_2 no longer change because the rate of formation of NO_2 is exactly equal to the rate of consumption of NO_2, and the rate of formation of N_2O_4 is exactly equal to the rate of consumption of N_2O_4. *Chemical equilibrium is a dynamic process*: the concentrations of each component remain constant, yet there is a flux back and forth between them (Figure 4.1.2).

Figure 4.1.2: These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant.

In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products. Plots showing how the reaction rates and concentrations change with respect to time are shown in Figure 4.1.1.

We can detect a state of equilibrium because the concentrations of reactants and products do not appear to change. However, it is important that we verify that the absence of change is due to equilibrium and not to a reaction rate that is so slow that changes in concentration are difficult to detect.

We use a double arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. For example, Figure 4.1.1 shows the reaction:

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \tag{4.1.2}$$

When we wish to speak about one particular component of a reversible reaction, we use a single arrow. For example, in the equilibrium shown in Figure 4.1.1, the rate of the reverse reaction

$$2\,NO_2(g) \rightarrow N_2O_4(g) \tag{4.1.3}$$

is equal to the rate of the forward reaction

$$N_2O_4(g) \rightarrow 2\,NO_2(g) \tag{4.1.4}$$

Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804; mostly known today for his role in the discovery and identification of oxygen) discovered a method of infusing water with carbon dioxide to make carbonated water. In 1772, Priestly published a paper entitled “Impregnating Water with Fixed Air.” The paper describes dripping oil of vitriol (today we call this sulfuric acid, but what a great way to describe sulfuric acid: “oil of vitriol” literally means “liquid nastiness”) onto chalk (calcium carbonate). The resulting CO_2 falls into the container of water beneath the vessel in which the initial reaction takes place; agitation helps the gaseous CO_2 mix into the liquid water.

$$H_2SO_4(l) + CaCO_3(s) \rightarrow CO_2(g) + H_2O(l) + CaSO_4(aq)$$

Carbon dioxide is slightly soluble in water. There is an equilibrium reaction that occurs as the carbon dioxide reacts with the water to form carbonic acid (H_2CO_3). Since carbonic acid is a weak acid, it can dissociate into protons (H^+) and hydrogen carbonate ions (HCO_3^-).

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

Today, CO_2 can be pressurized into soft drinks, establishing the equilibrium shown above. Once you open the beverage container, however, a cascade of equilibrium shifts occurs. First, the CO_2 gas in the air space on top of the bottle escapes, causing the equilibrium between gas-phase CO_2 and dissolved or aqueous CO_2 to shift, lowering the concentration of CO_2 in the soft drink. Less CO_2 dissolved in the liquid leads to carbonic acid decomposing to dissolved CO_2 and H_2O. The lowered carbonic acid concentration causes a shift of the final equilibrium. As long as the soft drink is in an open container, the CO_2 bubbles up out of the beverage, releasing the gas into the air (Figure 4.1.3). With the lid off the bottle, the CO_2 reactions are no longer at equilibrium and will continue until no more of the reactants remain. This results in a soft drink with a much lowered CO_2 concentration, often referred to as "flat."

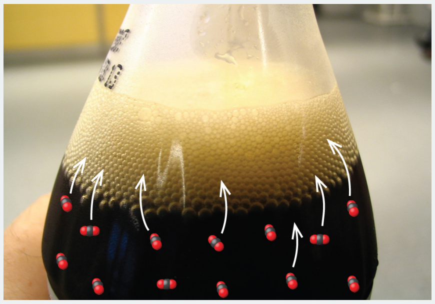

Figure 4.1.3: When a soft drink is opened, several equilibrium shifts occur. (credit: modification of work by "D Coetzee"/Flickr)

Sublimation of Bromine

Let us consider the evaporation of bromine as a second example of a system at equilibrium.

$$Br_2(l) \rightleftharpoons Br_2(g)$$

An equilibrium can be established for a physical change—like this liquid to gas transition—as well as for a chemical reaction. Figure 4.1.4 shows a sample of liquid bromine at equilibrium with bromine vapor in a closed container. When we pour liquid bromine into an empty bottle in which there is no bromine vapor, some liquid evaporates, the amount of liquid decreases, and the amount of vapor increases. If we cap the bottle so no vapor escapes, the amount of liquid and vapor will eventually stop changing and an equilibrium between the liquid and the vapor will be established. If the bottle were not capped, the bromine vapor would escape and no equilibrium would be reached.

Figure 4.1.4: An equilibrium is pictured between liquid bromine, $Br_2(l)$, the dark liquid, and bromine vapor, $Br_2(g)$, the orange gas. Because the container is sealed, bromine vapor cannot escape and equilibrium is maintained. (credit: http://images-of-elements.com/bromine.php).

Summary

A reaction is at equilibrium when the amounts of reactants or products no longer change. Chemical equilibrium is a dynamic process, meaning the rate of formation of products by the forward reaction is equal to the rate at which the products re-form reactants by the reverse reaction.

Glossary

equilibrium

in chemical reactions, the state in which the conversion of reactants into products and the conversion of products back into reactants occur simultaneously at the same rate; state of balance

reversible reaction

chemical reaction that can proceed in both the forward and reverse directions under given conditions

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4.2: Equilibrium Constants

Learning Objectives

- Derive reaction quotients from chemical equations representing homogeneous and heterogeneous reactions
- Calculate values of reaction quotients and equilibrium constants using concentrations
- Relate the magnitude of an equilibrium constant to properties of the chemical system

Now that we have a symbol ($\rightleftharpoons$) to designate reversible reactions, we will need a way to express mathematically how the amounts of reactants and products affect the equilibrium of the system. A general equation for a reversible reaction may be written as follows:

$$m\mathrm{A} + n\mathrm{B} + \rightleftharpoons x\mathrm{C} + y\mathrm{D} \tag{4.2.1}$$

4.2.1: Reaction Quotients

We can write the reaction quotient (Q) for this equation. When evaluated using concentrations, it is called Q_c. We use brackets to indicate molar concentrations of reactants and products.

$$Q_c = \frac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n} \tag{4.2.2}$$

The reaction quotient is equal to the molar concentrations of the products of the chemical equation (multiplied together) over the reactants (also multiplied together), with each concentration raised to the power of the coefficient of that substance in the balanced chemical equation. For example, the reaction quotient for the reversible reaction

$$2\,\mathrm{NO}_{2(g)} \rightleftharpoons \mathrm{N_2O}_{4(g)} \tag{4.2.3}$$

is given by this expression:

$$Q_c = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} \tag{4.2.4}$$

✓ Example 4.2.1: Writing Reaction Quotient Expressions

Write the expression for the reaction quotient for each of the following reactions:

a. $3\,\mathrm{O}_{2(g)} \rightleftharpoons 2\,\mathrm{O}_{3(g)}$
b. $\mathrm{N}_{2(g)} + 3\,\mathrm{H}_{2(g)} \rightleftharpoons 2\,\mathrm{NH}_{3(g)}$
c. $4\,\mathrm{NH}_{3(g)} + 7\,\mathrm{O}_{2(g)} \rightleftharpoons 4\,\mathrm{NO}_{2(g)} + 6\,\mathrm{H_2O}_{(g)}$

Solution

a. $Q_c = \frac{[\mathrm{O_3}]^2}{[\mathrm{O_2}]^3}$
b. $Q_c = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3}$
c. $Q_c = \frac{[\mathrm{NO_2}]^4[\mathrm{H_2O}]^6}{[\mathrm{NH_3}]^4[\mathrm{O_2}]^7}$

? Exercise 4.2.1

Write the expression for the reaction quotient for each of the following reactions:

a. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g)$
b. $\mathrm{C_4H_8}(g) \rightleftharpoons 2\,\mathrm{C_2H_4}(g)$
c. $2\,\mathrm{C_4H_{10}}(g) + 13\,\mathrm{O_2}(g) \rightleftharpoons 8\,\mathrm{CO_2}(g) + 10\,\mathrm{H_2O}(g)$

Answer a

$$Q_c = \frac{[\mathrm{SO_3}]^2}{[\mathrm{SO_2}]^2[\mathrm{O_2}]}$$

Answer b

$$Q_c = \frac{[\mathrm{C_2H_4}]^2}{[\mathrm{C_4H_8}]}$$

Answer c

$$Q_c = \frac{[\mathrm{CO_2}]^8[\mathrm{H_2O}]^{10}}{[\mathrm{C_4H_{10}}]^2[\mathrm{O_2}]^{13}}$$

The numeric value of Q_c for a given reaction varies; it depends on the concentrations of products and reactants present at the time when Q_c is determined. When pure reactants are mixed, Q_c is initially zero because there are no products present at that point. As the reaction proceeds, the value of Q_c increases as the concentrations of the products increase and the concentrations of the reactants simultaneously decrease (Figure 4.2.1). When the reaction reaches equilibrium, the value of the reaction quotient no longer changes because the concentrations no longer change.

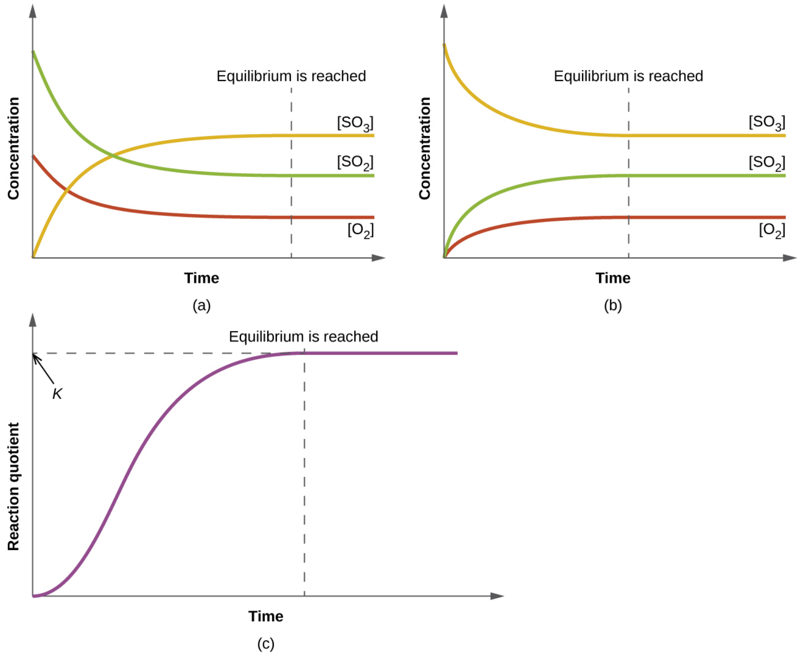

Figure 4.2.1: (a) The change in the concentrations of reactants and products is depicted as the $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g)$ reaction approaches equilibrium. (b) The change in concentrations of reactants and products is depicted as the reaction $2\,\mathrm{SO_3}(g) \rightleftharpoons 2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g)$ approaches equilibrium. (c) The graph shows the change in the value of the reaction quotient as the reaction approaches equilibrium.

4.2.2: The Law of Mass Action and the Equilibrium Constant K

When a mixture of reactants and products of a reaction reaches equilibrium at a given temperature, its reaction quotient always has the same value. This value is called the equilibrium constant (K) of the reaction at that temperature. As for the reaction quotient, when evaluated in terms of concentrations, it is noted as K_c.

That a reaction quotient always assumes the same value at equilibrium can be expressed as:

$$Q_c \text{ at equilibrium} = K_c = \frac{[\mathrm{C}]^x[\mathrm{D}]^y\ldots}{[\mathrm{A}]^m[\mathrm{B}]^n\ldots} \tag{4.2.5}$$

This equation is a mathematical statement of the law of mass action: When a reaction has attained equilibrium at a given temperature, the reaction quotient for the reaction always has the same value.

✓ Example 4.2.2: Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$2\,\mathrm{NO}_{2(g)} \rightleftharpoons \mathrm{N_2O}_{4(g)}$$

When 0.10 mol $\mathrm{NO_2}$ is added to a 1.0-L flask at 25 °C, the concentration changes so that at equilibrium, $[\mathrm{NO_2}]$ = 0.016 M and $[\mathrm{N_2O_4}]$ = 0.042 M.

a. What is the value of the reaction quotient before any reaction occurs?
b. What is the value of the equilibrium constant for the reaction?

Solution

a. Before any product is formed, $[\mathrm{NO_2}] = \frac{0.10\ \mathrm{mol}}{1.0\ \mathrm{L}} = 0.10\ M$, and $[\mathrm{N_2O_4}]$ = 0 M. Thus,

$$Q_c = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} = \frac{0}{0.10^2} = 0$$

b. At equilibrium, the value of the equilibrium constant is equal to the value of the reaction quotient. At equilibrium,

$$K_c = Q_c = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2.$$

The equilibrium constant is 1.6×10^2.

Note that dimensional analysis would suggest the unit for this K_c value should be M^{-1}. However, it is common practice to omit units for K_c values computed as described here, since it is the magnitude of an equilibrium constant that relays useful information. As will be discussed later in this module, the rigorous approach to computing equilibrium constants uses dimensionless quantities derived from concentrations instead of actual concentrations, and so K_c values are truly unitless.

? Exercise 4.2.2

For the reaction

$$2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g)$$

the concentrations at equilibrium are $[\mathrm{SO_2}]$ = 0.90 M, $[\mathrm{O_2}]$ = 0.35 M, and $[\mathrm{SO_3}]$ = 1.1 M. What is the value of the equilibrium constant, K_c?

Answer

K_c = 4.3

The magnitude of an equilibrium constant is a measure of the yield of a reaction when it reaches equilibrium. A large value for K_c indicates that equilibrium is attained only after the reactants have been largely converted into products. A small value of K_c—much less than 1—indicates that equilibrium is attained when only a small proportion of the reactants have been converted into products.

Once a value of K_c is known for a reaction, it can be used to predict directional shifts when compared to the value of Q_c. A system that is not at equilibrium will proceed in the direction that establishes equilibrium. The data in Figure 4.2.2 illustrate this. When heated to a consistent temperature, 800 °C, different starting mixtures of CO, $\mathrm{H_2O}$, $\mathrm{CO_2}$, and $\mathrm{H_2}$ react to reach compositions adhering to the same equilibrium (the value of Q_c changes until it equals the value of K_c). This value is 0.640, the equilibrium constant for the reaction under these conditions.

$$\mathrm{CO}(g) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g) + \mathrm{H_2}(g) \quad K_c = 0.640 \quad \mathrm{T} = 800^\circ\mathrm{C} \tag{4.2.6}$$

It is important to recognize that an equilibrium can be established starting either from reactants or from products, or from a mixture of both. For example, equilibrium was established from Mixture 2 in Figure 4.2.2 when the products of the reaction were heated in a closed container. In fact, one technique used to determine whether a reaction is truly at equilibrium is to approach equilibrium starting with reactants in one experiment and starting with products in another. If the same value of the reaction quotient is observed when the concentrations stop changing in both experiments, then we may be certain that the system has reached equilibrium.

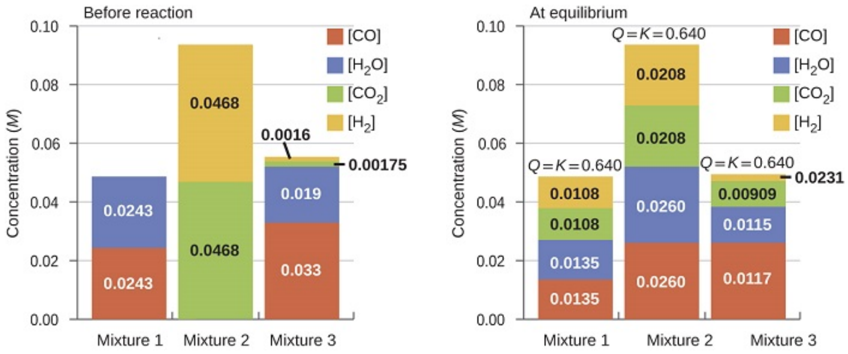

Figure 4.2.2: Concentrations of three mixtures are shown before and after reaching equilibrium at 800 °C for the so-called water gas shift reaction (Equation 4.2.6).

Example 4.2.3: Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

with $K_c = 0.64$. Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[CO]_i$	0.0203 *M*	0.011 *M*	0.0094 *M*
$[H_2O]_i$	0.0203 *M*	0.0011 *M*	0.0025 *M*
$[CO_2]_i$	0.0040 *M*	0.037 *M*	0.0015 *M*
$[H_2]_i$	0.0040 *M*	0.046 *M*	0.0076 *M*

Solution

Experiment 1:

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0040)(0.0040)}{(0.0203)(0.0203)} = 0.039.$$

$Q_c < K_c$ (0.039 < 0.64)

The reaction will shift to the right.

Experiment 2:

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will shift to the left.

Experiment 3:

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will shift to the right.

Exercise 4.2.3

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

(a) A 1.00-L flask containing 0.0500 mol of NO(g), 0.0155 mol of Cl_2(g), and 0.500 mol of NOCl:

$$2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{NOCl}(g) \quad K_c = 4.6 \times 10^4$$

(b) A 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \quad K_c = 0.060$$

(c) A 2.00-L flask containing 230 g of SO_3(g):

$$2\,\mathrm{SO_3}(g) \rightleftharpoons 2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \quad K_c = 0.230$$

Answer a

Q_c = 6.45 × 10^3, shifts right.

Answer b

Q_c = 0.12, shifts left.

Answer c

Q_c = 0, shifts right

4.2.3: K is a Unitless Quantity

In Example 4.2.2, it was mentioned that the common practice is to omit units when evaluating reaction quotients and equilibrium constants. It should be pointed out that using concentrations in these computations is a convenient but simplified approach that sometimes leads to results that seemingly conflict with the law of mass action. For example, equilibria involving aqueous ions often exhibit equilibrium constants that vary quite significantly (are *not* constant) at high solution concentrations. This may be avoided by computing K_c values using the *activities* of the reactants and products in the equilibrium system instead of their concentrations. The activity of a substance is a measure of its effective concentration under specified conditions. While a detailed discussion of this important quantity is beyond the scope of an introductory text, it is necessary to be aware of a few important aspects:

- Activities are dimensionless (**unitless**) quantities and are in essence “adjusted” concentrations.
- For relatively dilute solutions, a substance's activity and its molar concentration are roughly equal.
- Activities for pure condensed phases (solids and liquids) are equal to 1.
- Activities for solvents in dilute solutions are equal to 1.

As a consequence of this last consideration, Q_c and K_c expressions do not contain terms for solids or liquids or solvents in dilute solutions (being numerically equal to 1, these terms have no effect on the expression's value). Several examples of equilibria yielding such expressions will be encountered in this section.

4.2.4: Homogeneous Equilibria

A homogeneous equilibrium is one in which all of the reactants and products are present in a single solution (by definition, a homogeneous mixture). In this chapter, we will concentrate on the two most common types of homogeneous equilibria: those occurring in liquid-phase solutions and those involving exclusively gaseous species. Reactions between solutes in liquid solutions belong to one type of homogeneous equilibria. The chemical species involved can be molecules, ions, or a mixture of both. Several examples are provided here:

Example 1

$$\mathrm{C_2H_2}(aq) + 2\,\mathrm{Br_2}(aq) \rightleftharpoons \mathrm{C_2H_2Br_4}(aq) \tag{4.2.7}$$

with associated equilibrium constant

$$K_c = \frac{[C_2H_2Br_4]}{[C_2H_2][Br_2]^2} \tag{4.2.8}$$

Example 2

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \tag{4.2.9}$$

with associated equilibrium constant

$$K_c = \frac{[I_3^-]}{[I_2][I^-]} \tag{4.2.10}$$

Example 3

$$Hg_2^{2+}(aq) + NO_3^-(aq) + 3\,H_3O^+(aq) \rightleftharpoons 2\,Hg^{2+}(aq) + HNO_2(aq) + 4\,H_2O(l) \tag{4.2.11}$$

with associated equilibrium constant

$$K_c = \frac{[Hg^{2+}]^2[HNO_2]}{[Hg_2^{2+}][NO_3^-][H_3O^+]^3} \tag{4.2.12}$$

Example 4

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \tag{4.2.13}$$

with associated equilibrium constant

$$K_c = \frac{[H_3O^+][F^-]}{[HF]} \tag{4.2.14}$$

Example 5

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{4.2.15}$$

with associated equilibrium constant

$$K_c = \frac{[NH_4^+][OH^-]}{[NH_3]} \tag{4.2.16}$$

In each of these examples, the equilibrium system is an aqueous solution, as denoted by the *aq* annotations on the solute formulas. Since H_2O(l) is the solvent for these solutions, it **does not** appear as a term in the K_c expression, as discussed earlier, even though it may also appear as a reactant or product in the chemical equation.

Reactions in which all reactants and products are gases represent a second class of homogeneous equilibria. We use molar concentrations in the following examples, but we will see shortly that partial pressures of the gases may be used as well:

Example 1

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g) \tag{4.2.17}$$

with associated equilibrium constant

$$K_c = \frac{[C_2H_4][H_2]}{[C_2H_6]} \tag{4.2.18}$$

Example 2

$$3\,O_2(g) \rightleftharpoons 2\,O_3(g) \tag{4.2.19}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{O_3}]^2}{[\mathrm{O_2}]^3} \tag{4.2.20}$$

Example 3

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \tag{4.2.21}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3} \tag{4.2.22}$$

Example 4

$$\mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(g) \tag{4.2.23}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{CO_2}]^3[\mathrm{H_2O}]^4}{[\mathrm{C_3H_8}][\mathrm{O_2}]^5} \tag{4.2.24}$$

Note that the concentration of $\mathrm{H_2O}_{(g)}$ has been included in the last example because water is not the solvent in this gas-phase reaction and its concentration (and activity) changes.

Summary

For any reaction that is at equilibrium, the reaction quotient *Q* is equal to the equilibrium constant *K* for the reaction. If a reactant or product is a pure solid, a pure liquid, or the solvent in a dilute solution, the concentration of this component does not appear in the expression for the equilibrium constant. At equilibrium, the values of the concentrations of the reactants and products are constant. Their particular values may vary depending on conditions, but the value of the reaction quotient will always equal *K*. We can decide whether a reaction is at equilibrium by comparing the reaction quotient with the equilibrium constant for the reaction.

4.2.5: Key Equations

- $Q = \frac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n} \quad \text{where } m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$

Glossary

equilibrium constant (*K*)

value of the reaction quotient for a system at equilibrium

heterogeneous equilibria

equilibria between reactants and products in different phases

homogeneous equilibria

equilibria within a single phase

K_c

equilibrium constant for reactions based on concentrations of reactants and products

law of mass action

when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

reaction quotient (*Q*)

ratio of the product of molar concentrations (or pressures) of the products to that of the reactants, each concentration (or pressure) being raised to the power equal to the coefficient in the equation

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4.3: Gas Phase Equilibria and Heterogeneous Systems

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.

Whenever gases are involved in a reaction, the partial pressure of each gas can be used instead of its concentration in the equation for the reaction quotient because the partial pressure of a gas is directly proportional to its concentration at constant temperature.

Equilibrium Constant Expressions for Systems that Contain Gases

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 $aA + bB \rightleftharpoons cC + dD$, 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):

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \tag{4.3.1}$$

Thus K_p for the decomposition of N_2O_4 (Equation 15.1) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \tag{4.3.2}$$

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.

This relationship between K_C and K_P can be derived from the ideal gas equation, where M is the molar concentration of gas, $\frac{n}{V}$.

$$PV = nRT \tag{4.3.3}$$

$$P = \left(\frac{n}{V}\right) RT \tag{4.3.4}$$

$$= MRT \tag{4.3.5}$$

Thus, at constant temperature, the pressure of a gas is **directly proportional** to its concentration. Using the partial pressures of the gases, we can write the reaction quotient for the system

$$\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g) \tag{4.3.6}$$

by following the same guidelines for deriving concentration-based expressions:

$$Q_P = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}} \tag{4.3.7}$$

In this equation we use Q_P to indicate a reaction quotient written with partial pressures: $P_{\mathrm{C_2H_6}}$ is the partial pressure of C_2H_6; $P_{\mathrm{H_2}}$, the partial pressure of H_2; and $P_{\mathrm{C_2H_6}}$, the partial pressure of C_2H_4. At equilibrium:

$$K_P = Q_P = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}} \tag{4.3.8}$$

The subscript P in the symbol K_P designates an equilibrium constant derived using partial pressures instead of concentrations. The equilibrium constant, K_P, is still a constant, but its numeric value may differ from the equilibrium constant found for the same reaction by using concentrations.

Conversion between a value for K_c, an equilibrium constant expressed in terms of concentrations, and a value for K_P, an equilibrium constant expressed in terms of pressures, is straightforward (a K or Q without a subscript could be either concentration or pressure).

The equation relating K_c and K_P is derived as follows. For the gas-phase reaction:

$$m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D} \tag{4.3.9}$$

with

$$\begin{aligned} K_P &= \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n} && (4.3.10) \\ &= \frac{([\mathrm{C}] \times RT)^x ([\mathrm{D}] \times RT)^y}{([\mathrm{A}] \times RT)^m ([\mathrm{B}] \times RT)^n} && (4.3.11) \\ &= \frac{[\mathrm{C}]^x [\mathrm{D}]^y}{[\mathrm{A}]^m [\mathrm{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} && (4.3.12) \\ &= K_c (RT)^{(x+y)-(m+n)} && (4.3.13) \\ &= K_c (RT)^{\Delta n} && (4.3.14) \end{aligned}$$

The relationship between K_c and K_P is

$$\backslash \mathrm{K}_P = K_c(RT)^{\Delta n} \tag{4.3.15}$$

In this equation, Δn is the difference between the sum of the coefficients of the *gaseous* products and the sum of the coefficients of the *gaseous* reactants in the reaction (the change in moles of gas between the reactants and the products). For the gas-phase reaction $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$, we have

$$\Delta n = (x + y) - (m + n) \tag{4.3.16}$$

✓ Example 4.3.1: Calculation of K_P

Write the equations for the conversion of K_c to K_P for each of the following reactions:

a. $\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g)$
b. $\mathrm{CO}(g) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g) + \mathrm{H_2}(g)$
c. $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g)$
d. K_c is equal to 0.28 for the following reaction at 900 °C:

$$\mathrm{CS_2}(g) + 4\,\mathrm{H_2}(g) \rightleftharpoons \mathrm{CH_4}(g) + 2\,\mathrm{H_2S}(g) \tag{4.3.17}$$

What is K_P at this temperature?

Solution

(a) $\Delta n = (2) - (1) = 1$

$$K_P = K_c\ (RT)^{\Delta n} = K_c\ (RT)^1 = K_c\ (RT)$$

(b) $\Delta n = (2) - (2) = 0$

$$K_P = K_c\ (RT)^{\Delta n} = K_c\ (RT)^0 = K_c$$

(c) $\Delta n = (2) - (1 + 3) = -2$

$$K_P = K_c\ (RT)^{\Delta n} = K_c\ (RT)^{-2} = \frac{K_c}{(RT)^2}$$

d) $K_P = K_c\ (\mathrm{RT})^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0 \times 10^{-5}$

? Exercise 4.3.1

Write the equations for the conversion of K_c to K_P for each of the following reactions, which occur in the gas phase:

a. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g)$

b. $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$
c. $C_3H_8(g) + 5\,O_2(g) \rightleftharpoons 3\,CO_2(g) + 4\,H_2O(g)$
d. At 227 °C, the following reaction has K_c = 0.0952:

$$CH_3OH(g) \rightleftharpoons CO(g) + 2\,H_2(g) \tag{4.3.18}$$

What would be the value of K_P at this temperature?

Answer a

$K_P = K_c\,(RT)^{-1}$

Answer b

$K_P = K_c\,(RT)$

Answer c

$K_P = K_c\,(RT)$;

Answer d

160 or 1.6×10^2

Video Discussing Converting Kc to Kp: https://youtu.be/_2WVnlqXrV4

Heterogeneous Equilibria

A heterogeneous equilibrium is a system in which reactants and products are found in two or more phases. The phases may be any combination of solid, liquid, or gas phases, and solutions. When dealing with these equilibria, remember that solids and pure liquids do not appear in equilibrium constant expressions (the activities of pure solids, pure liquids, and solvents are 1).

Some heterogeneous equilibria involve chemical changes:

Example 1

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq) \tag{4.3.19}$$

with associated equilibrium constant

$$K_c = [Pb^{2+}][Cl^-]^2 \tag{4.3.20}$$

Example 2

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \tag{4.3.21}$$

with associated equilibrium constant

$$K_c = \frac{1}{P_{CO_2}} \tag{4.3.22}$$

Example 3

$$\mathrm{C}(s)+2\,\mathrm{S}(g)\rightleftharpoons\mathrm{CS}_2(g) \tag{4.3.23}$$

with associated equilibrium constant

$$K_c=\frac{\mathrm{P}_{\mathrm{CS}_2}}{\mathrm{P}_{\mathrm{S}}^2} \tag{4.3.24}$$

Other heterogeneous equilibria involve phase changes, for example, the evaporation of liquid bromine, as shown in the following equation:

$$\mathrm{Br}_2(l)\rightleftharpoons\mathrm{Br}_2(g) \tag{4.3.25}$$

with associated equilibrium constant

$$K_c=P_{\mathrm{Br}_2} \tag{4.3.26}$$

Summary

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 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.

- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.
- Equilibrium constant expression for reactions involving gases using partial pressures:

$$K_p=\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \tag{4.3.27}$$

- Relationship between K_p and K:

$$K_p=K(RT)^{\Delta n} \tag{4.3.28}$$

4.4: Shifting Equilibria - Le Chatelier’s Principle

Learning Objectives

- Predict whether reactants or products are favored in a given reaction based on the equilibrium constant
- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier’s principle

Reversible reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). In this section, you will learn to predict whether reactants or products are favored at equilbrium, and how to predict the direction a reaction will proceed when its equilibrium is disturbed.

4.4.1: Relating K to the Reaction Mixture Composition

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:

$$\mathrm{H_2(g) + D_2(g) \rightleftharpoons 2\,HD(g)}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]}$$

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 4.4.1 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 ??? and ???), 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.

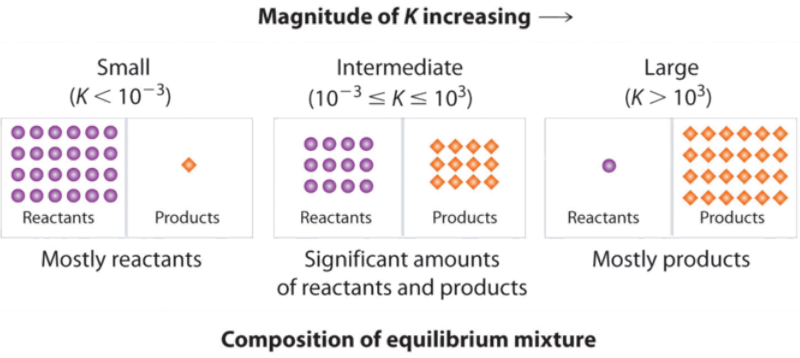

Figure 4.4.1: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

> *A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.*

✓ Example 4.4.1

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. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

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 $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K \ll 10^{-3}$, 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 4.4.1

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3\,\mathrm{H_2(g)} + \mathrm{N_2(g)} \rightleftharpoons 2\,\mathrm{NH_3(g)}$$

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

Video which Discusses What Does K Tell us About a Reaction?: https://youtu.be/39-456o3O_4

4.4.2: Predicting the Direction of a Reversible Reaction

We next address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K. If a system at equilibrium is subjected to a perturbance or stress (such as a change in concentration) the position of equilibrium changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K. To re-establish equilibrium, the system will either shift toward the products (if $Q < K$) or the reactants (if $Q > K$) until Q returns to the same value as K.

This process is described by Le Chatelier's principle: When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in Q; the reaction will shift to re-establish $Q = K$.

Le Chatelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of Q and K for the system to predict the changes.

> A chemical system at equilibrium can be **temporarily** shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.

The stress on the system in Figure 4.4.1 is the reduction of the equilibrium concentration of SCN$^-$ (lowering the concentration of one of the reactants would cause Q to be larger than K). As a consequence, Le Chatelier's principle leads us to predict that the concentration of Fe(SCN)$^{2+}$ should decrease, increasing the concentration of SCN$^-$ part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.

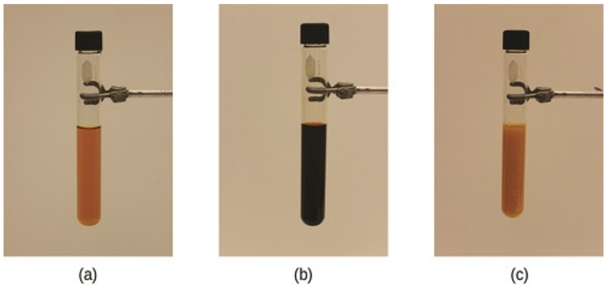
(a) (b) (c)

Figure 4.4.1: (a) The test tube contains 0.1 M Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red Fe(SCN)$^{2+}$ ion. $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$. *(c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN− as the white solid AgSCN.* $Ag^+(aq) + SCN^-(aq) \rightleftharpoons AgSCN(s)$ *The decrease in the SCN− concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the Fe(SCN)$^{2+}$. (credit: modification of work by Mark Ott).*

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2\,HI_{(g)} \tag{4.4.1}$$

$$K_c = 50.0 \text{ at } 400^\circ\text{C} \tag{4.4.2}$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[H_2] = [I_2] = 0.221\ M$ and $[HI] = 1.563\ M$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If H_2 is introduced into the system so quickly that its concentration doubles before it begins to react (new $[H_2] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which

- $[H_2] = 0.374\ M$,
- $[I_2] = 0.153\ M$, and
- $[HI] = 1.692\ M$.

This gives:

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.692)^2}{(0.374)(0.153)} = 50.0 = K_c \tag{4.4.3}$$

We have stressed this system by introducing additional H_2. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess H_2, reducing the amount of uncombined I_2, and forming additional HI.

4.4.3: 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.

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:

$$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g) \tag{4.4.4}$$

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:

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \tag{4.4.5}$$

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.

4.4.4: 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.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \quad \Delta H = -9.4 \text{ kJ (exothermic)} \tag{4.4.6}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) + \text{heat} \tag{4.4.7}$$

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

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \quad \Delta H = 57.20 \text{ kJ} \tag{4.4.8}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\text{heat} + N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \tag{4.4.9}$$

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.

4.4.5: Catalysts Do Not Affect Equilibrium

As we learned during our study of kinetics, a catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations.

The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \tag{4.4.10}$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

Fritz Haber

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures.

The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery.

For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements. The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \tag{4.4.11}$$

Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008. The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen (N_2) is nutritionally unavailable due the tremendous stability of the nitrogen-nitrogen triple bond. For plants to use atmospheric nitrogen, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation).

In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, “During peace time a scientist belongs to the World, but during war time he belongs to his country.”[1] Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.

Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood.

To be practical, an industrial process must give a large yield of product relatively quickly. One way to increase the yield of ammonia is to increase the pressure on the system in which N_2, H_2, and NH_3 are at equilibrium or are coming to equilibrium.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \tag{4.4.12}$$

The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of N_2, H_2, and NH_3 will increase the yield of ammonia, at low temperatures, the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2, no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:

$$N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g) \quad \Delta H = -92.2\text{ kJ} \tag{4.4.13}$$

Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favor the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst. The net effect of the catalyst on the reaction is to cause equilibrium to be reached more rapidly. In the commercial production of ammonia, conditions of about 500 °C, 150–900 atm, and the presence of a catalyst are used to give the best compromise among rate, yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures.

Summary

The magnitude of an equilibrium constant will allow you to predict whether the reactants or products will be in excess when the system is at 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.

Table 4.4.1: 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. 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

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- **13.4: Shifting Equilibria - Le Chatelier’s Principle** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.
- **13.3: Equilibrium Constants** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.
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4.5: Calculating Equilibrium Constants and Equilibrium Concentrations

Learning Objectives

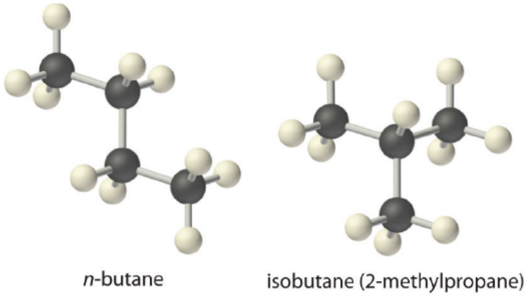
- To determine the equilibrium constant K from equilibrium concentrations.
- To calculate the equilibrium concentrations in a reaction when initial concentrations and K are know.

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

We'll begin by considering the 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:

$$\text{n}-\text{butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{4.5.1}$$

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,

$$K = \frac{[isobutane]}{[n\text{-}butane]} = 0.041\ M = 2.6 \tag{4.5.2}$$

Thus the equilibrium constant for the reaction as written is 2.6.

Example 4.5.1

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:

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

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.

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 use the relationship derived previously

$$K_p = K(RT)^{\Delta n} \tag{4.5.3}$$

where $\Delta n = 2 - 3 = -1$:

$$K_p = K(RT)^{\Delta n}$$

$$K_p = 7.9 \times 10^4 [(0.08206\ L \cdot atm/mol \cdot K)(800 K)]^{-1}$$

$$K_p = 1.2 \times 10^3$$

? Exercise 4.5.1

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

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

$K = 48.8$ and $K_p = 48.8$

Since the law of mass action is the only equation we have to describe the relationship between K_c and the concentrations of reactants and products, any problem that requires us to solve for K_c must provide enough information to determine the reactant and product concentrations at equilibrium. Armed with the concentrations, we can solve the equation for K_c, as it will be the only unknown.

Example 4.5.1 showed us how to determine the equilibrium constant of a reaction if we know the concentrations of reactants and products at equilibrium. The following example shows how to use the stoichiometry of the reaction and a combination of initial concentrations and equilibrium concentrations to determine an equilibrium constant. This technique, commonly called an ICE table—for **I**nitial, **C**hange, and **E**quilibrium–will be helpful in solving many equilibrium problems. A chart is generated beginning with the equilibrium reaction in question. Underneath the reaction the **initial concentrations** of the reactants and products are listed—these conditions are usually provided in the problem and we consider no shift toward equilibrium to have happened. The next row of data is the **change** that occurs as the system shifts toward equilibrium. If the reaction shifts to the right, the change will be positive for the products (products are generated) and negative for the reactants (reactants are consumed). Importantly, we must consider the reaction stoichiometry when determining the quantities in the change row. If a reaction generates two moles of product for every mole of reactant, we must multiply the change quantity by two for the product side. The last row contains the concentrations once equilibrium has been reached, and will be the sum of the initial and change rows. Example 4.5.2 demonstrates how to use an ICE table to calculate the equilibrium constant.

✓ Example 4.5.2

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:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

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 4.5.2

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

$K = 0.105$ and $K_p = 2.61 \times 10^{-5}$

A Video Disucssing Using ICE Tables to find Kc: https://youtu.be/CwQmO4M2s64

Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we will again consider a system that contains only a single product and a single reactant, the conversion of n-butane to isobutane (Equation 4.5.1), 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 an ICE table, just as we did in Example $4.5.2$.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{4.5.4}$$

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. We know this reaction will generate products as it approaches equilibrium because initially no isobutane is present. 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.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{4.5.5}$$

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,

$$K=\frac{[\text{isobutane}]}{[\text{n-butane}]}=\frac{x}{1.00-x}=2.6 \tag{4.5.6}$$

Rearranging and solving for x,

$$x = 2.6(1.00 - x) = 2.6 - 2.6x \tag{4.5.7}$$

$$x + 2.6x = 2.6 \tag{4.5.8}$$

$$x = 0.72 \tag{4.5.9}$$

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:

$$[\text{n-butane}]_f = (1.00 - x)M = (1.00 - 0.72)M = 0.28\ M \tag{4.5.10}$$

$$[\text{isobutane}]_f = (0.00 + x)M = (0.00 + 0.72)M = 0.72\ M \tag{4.5.11}$$

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:

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \left(\frac{0.72\ \cancel{M}}{0.28\ \cancel{M}}\right) = 2.6 \tag{4.5.12}$$

This is the same K we were given, so we can be confident of our results.

Example $4.5.3$ illustrates a common type of equilibrium problem that you are likely to encounter.

✓ Example $4.5.3$: The water–gas shift reaction

The water–gas shift reaction is important in several chemical processes, such as the production of H_2 for fuel cells. This reaction 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?

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,

$$\frac{x}{(0.0150-x)}=(0.106)^{1/2}=0.326$$

$$x=(0.326)(0.0150)-0.326x$$

$$1.326x=0.00489$$

$$x=0.00369=3.69\times10^{-3}$$

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 $4.5.3$

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 $4.5.3$, 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. One way we can solve for x in the K expression is using the **quadratic formula**. Such a case is described in Example $4.5.4$.

✓ Example $4.5.4$

In the water–gas shift reaction shown in Example $4.5.3$, a sample containing 0.632 M CO2 and 0.570 M 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?

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 4.5.3, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.202x + x^2)$$

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 4.5.4

The reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K = 54$ at 425°C, is shown below.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

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. These types of equilibrium problems are described in the next section.

A Video Discussing Using ICE Tables to find Eq. Concentrations & Kc: https://youtu.be/vGQWZHlNWyM

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 (i.e. an ICE table) to obtain the final concentrations of all species at equilibrium.

4.6: Calculating Equilibrium Concentrations with the "x-is-small" Approximation

Learning Objectives

- Identify systems where the x-is-small approximation can be used to solve equilibrium problems
- Manipulate initial concentrations to start at the "all reactant" or "all product" condition

Sometimes it is possible to use chemical insight to find solutions to equilibrium problems without actually solving a quadratic (or more complicated) equation. Most of these cases involve reactions for which the equilibrium constant is either very small ($K \leq 10^{-3}$) or very large ($K \geq 10^{3}$).

Recall that a small K_c means that very little of the reactants form products. This means that the change in the concentration in the system (defined as x) is essentially negligible compared with the initial concentration of a substance. Knowing this simplifies the calculations dramatically.

The "x-is-small" approximation is based on the idea that if the system can be arranged so it starts “close” to equilibrium, then if the change (x) is small compared to any initial concentrations, it can be neglected. Small is usually defined as resulting in an error of less than 5%.

$$\%\ change = \frac{x}{initial\ concentration} \times 100\%$$

Example $4.6.1$ demonstrates how the x-is-small approximation is used to simplify an equilibrium problem.

Example $4.6.1$: x-is-Small Approximation with "All Reactant" Initial Condition

What are the concentrations at equilibrium of a 0.15 M solution of HCN?

$$\mathrm{HCN}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{CN}^-(aq) \qquad K_c = 4.9 \times 10^{-10} \tag{4.6.1}$$

Solution

Using “x” to represent the concentration of each product at equilibrium gives this ICE table.

	$HCN(aq) \rightleftharpoons$	$H^+(aq)$ +	$CN^-(aq)$
Initial concentration (M)	0.15	0	0
Change (M)	$-x$	x	x
Equilibrium concentration (M)	$0.15 - x$	x	x

The exact solution may be obtained using the quadratic formula with

$$K_c = \frac{(x)(x)}{0.15 - x} \tag{4.6.2}$$

solving

$$x^2 + 4.9 \times 10^{-10} - 7.35 \times 10^{-11} = 0 \tag{4.6.3}$$

$$x = 8.56 \times 10^{-6}\ M\ (3\ \text{sig. figs.}) = 8.6 \times 10^{-6}\ M\ (2\ \text{sig. figs.}) \tag{4.6.4}$$

Thus $[H^+] = [CN^-] = x = 8.6 \times 10^{-6}\ M$ and $[HCN] = 0.15 – x = 0.15\ M$.

In this case, chemical intuition can provide a simpler solution. From the equilibrium constant and the initial conditions, x must be small compared to 0.15 M. More formally, if $x \ll 0.15$, then $0.15 – x \approx 0.15$. If this assumption is true, then it simplifies obtaining x

$$K_c = \frac{(x)(x)}{0.15 - x} \approx \frac{x^2}{0.15} \tag{4.6.5}$$

$$4.9 \times 10^{-10} = \frac{x^2}{0.15} \tag{4.6.6}$$

$$x^2 = (0.15)(4.9 \times 10^{-10}) = 7.4 \times 10^{-11} \tag{4.6.7}$$

$$x = \sqrt{7.4 \times 10^{-11}} = 8.6 \times 10^{-6}\ M \tag{4.6.8}$$

In this example, solving the exact (quadratic) equation and using approximations gave the same result to two significant figures. While most of the time the approximation is a bit different from the exact solution, as long as the error is less than 5%, the approximate solution is considered valid. In this problem, the 5% applies to IF $(0.15 – x) \approx 0.15\ M$, so if

$$\frac{x}{0.15} \times 100\% = \frac{8.6 \times 10^{-6}}{0.15} \times 100\% = 0.006\% \tag{4.6.9}$$

is less than 5%, as it is in this case, the assumption is valid. The approximate solution is thus a valid solution.

? Exercise 4.6.1

What are the equilibrium concentrations in a 0.25 M NH_3 solution?

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_c = 1.8 \times 10^{-5}$$

Assume that x is much less than 0.25 M and calculate the error in your assumption.

Answer

$[OH^-] = [NH_4^+] = 0.0021\ M$; $[NH_3]$ = 0.25 M, error = 0.84%

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 ($K \geq 10^3$). 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. If the initial concentrations of only the reactants are given, we use stoichiometry to predict the maximum amount of product that could be formed in the reaction. We use these adjusted concentrations as the "initial" conditions of the reaction in the ICE table. This approach is illustrated in Example 4.6.2.

✓ Example 4.6.2: x-is-Small Approximation with "All Product" Initial Condition

Copper(II) ions form a complex ion in the presence of ammonia

$$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq) \qquad K_c = 5.0 \times 10^{13} = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}(\text{aq})][NH_3]^4} \tag{4.6.10}$$

If 0.010 mol Cu^{2+} is added to 1.00 L of a solution that is 1.00 M NH_3 what are the concentrations when the system comes to equilibrium?

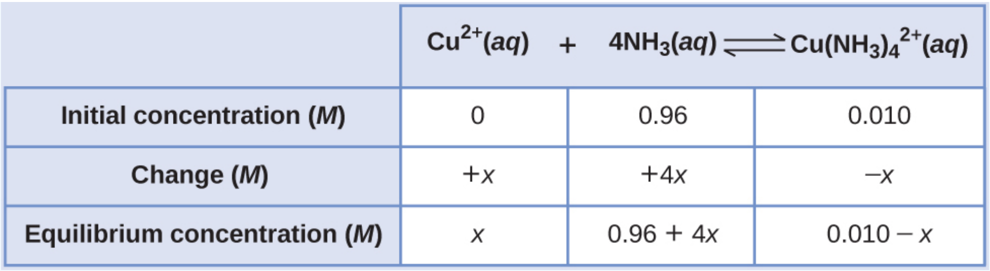
Solution The initial concentration of copper(II) is 0.010 M. The equilibrium constant is very large so it would be better to start with as much product as possible because “all products” is much closer to equilibrium than “all reactants.” Note that Cu^{2+} is the limiting reactant; if all 0.010 M of it reacts to form product the concentrations would be

$$[Cu^{2+}] = 0.010 - 0.010 = 0\ M \tag{4.6.11}$$

$$[Cu(NH_3)_4^{2+}] = 0.010\ M \tag{4.6.12}$$

$$[NH_3] = 1.00 - 4 \times 0.010 = 0.96\ M \tag{4.6.13}$$

Using these “shifted” values as initial concentrations with x as the free copper(II) ion concentration at equilibrium gives this ICE table.



	$Cu^{2+}(aq)$ +	$4NH_3(aq) \rightleftharpoons$	$Cu(NH_3)_4{}^{2+}(aq)$
Initial concentration (*M*)	0	0.96	0.010
Change (*M*)	$+x$	$+4x$	$-x$
Equilibrium concentration (*M*)	x	$0.96 + 4x$	$0.010 - x$

Since we are starting close to equilibrium, *x* should be small so that

$$0.96 + 4x \approx 0.96\ M$$
$$0.010 - x \approx 0.010\ M$$
$$K_c = \frac{(0.010 - x)}{x(0.96 - 4x)^4} \approx \frac{(0.010)}{x(0.96)^4} = 5.0 \times 10^{13}$$
$$x = \frac{(0.010)}{K_c(0.96)^4} = 2.4 \times 10^{-16}\ M$$

Select the smallest concentration for the 5% rule.

$$\frac{2.4 \times 10^{-16}}{0.010} \times 100\% = 2 \times 10^{-12}\%$$

This is much less than 5%, so the assumptions are valid. The concentrations at equilibrium are

$$[Cu^{2+}] = x = 2.4 \times 10^{-16}\ M$$
$$[NH_3] = 0.96 - 4x = 0.96\ M$$
$$[Cu(NH_3)_4^{2+}] = 0.010 - x = 0.010\ M$$

By starting with the maximum amount of product, this system was near equilibrium and the change (*x*) was very small. With only a small change required to get to equilibrium, the equation for *x* was greatly simplified and gave a valid result well within the 5% error maximum.

Exercise 4.6.2

What are the equilibrium concentrations when 0.25 mol Ni^{2+} is added to 1.00 L of 2.00 *M* NH_3 solution?

$$Ni^{2+}(aq) + 6\,NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq)$$

with $K_c = 5.5 \times 10^8$.

With such a large equilibrium constant, first form as much product as possible, then assume that only a small amount (*x*) of the product shifts left. Calculate the error in your assumption.

Answer

$[Ni(NH_3)_6^{2+}] = 0.25\ M$, $[NH_3] = 0.50\ M$, $[Ni^{2+}] = 2.9 \times 10^{-8}\ M$, error = $1.2 \times 10^{-5}\%$

Summary

When given the equilibrium constant and the initial concentrations, we can solve for the concentrations at equilibrium. When the equilibrium constant K is very small or very large, the mathematical operations can be simplified using the x-is-small approximation. When using the approximation, the x value from the equilibrium calculation should be less than 5% of any of the initial concentrations.

4.7: Equilibrium Constant Manipulations

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, earlier this chapter we considered the general, reversible reaction:

$$m\mathrm{A} + n\mathrm{B} + \rightleftharpoons x\mathrm{C} + y\mathrm{D} \tag{4.7.1}$$

We defined the equilibrium constant (K) for this equation to be:

$$K = \frac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n} \tag{4.7.2}$$

where each of the concentrations is the equilibrium concentration. If we write the reaction in reverse, we obtain the following:

$$xC + yD \rightleftharpoons mA + nB \tag{4.7.3}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^m[B]^n}{[C]^x[D]^y} \tag{4.7.4}$$

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 $\mathrm{N_2O_4} \rightleftharpoons 2\,\mathrm{NO_2}$ is as follows:

$$K = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]} \tag{4.7.5}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K′ is given by the inverse expression:

$$K' = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} \tag{4.7.6}$$

Consider another example, the formation of water:

$$2\,\mathrm{H_2(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{H_2O(g)}.$$

Because $\mathrm{H_2}$ is a good reductant and $\mathrm{O_2}$ 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 $\mathrm{O_2}$ and $\mathrm{H_2}$, 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 $\mathrm{H_2}$ and $\mathrm{O_2}$.

> *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

$$2\,\mathrm{NO_2} \rightleftharpoons \mathrm{N_2O_4}$$

as

$$\mathrm{NO_2} \rightleftharpoons \tfrac{1}{2}\mathrm{N_2O_4}$$

with the equilibrium constant K″ is as follows:

$$K'' = \frac{[\mathrm{N_2O_4}]^{1/2}}{[\mathrm{NO_2}]} \tag{4.7.7}$$

The values for K′ (Equation 4.7.6) and K″ are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{4.7.8}$$

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.

A Video Discussing Relationships Involving Equilibrium Constants: https://youtu.be/2vZDpXX1zr0

✓ Example 4.7.1: 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. $\mathrm{\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)}$

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 $N_{2(g)}$ with $H_{2(g)}$ to produce $NH_{3(g)}$ 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 4.7.1

At 527°C, the equilibrium constant for the reaction

$$2\,\mathrm{SO_2(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{SO_3(g)}$$

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$\mathrm{SO_3(g)} \rightleftharpoons \mathrm{SO_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)}$$

Answer

3.6×10^{-3}

Equilibrium Constant Expressions for the Sums of Reactions

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 $\mathrm{N_2}$ with $\mathrm{O_2}$ to give $\mathrm{NO_2}$. This reaction is an important source of the $\mathrm{NO_2}$ that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps. In the first reaction (step 1), $\mathrm{N_2}$ reacts with $\mathrm{O_2}$ at the high temperatures inside an internal combustion engine to give NO. The released NO then reacts with additional $\mathrm{O_2}$ to give $\mathrm{NO_2}$ (step 2). The equilibrium constant for each reaction at 100°C is also given.

$$\mathrm{N_2(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{NO(g)} \qquad K_1 = 2.0 \times 10^{-25}$$

$$2\,\mathrm{NO(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{NO_2(g)} \quad K_2 = 6.4 \times 10^{9}$$

Summing reactions (step 1) and (step 2) gives the overall reaction of N_2 with O_2:

$$\mathrm{N_2(g)} + 2\,\mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{NO_2(g)} \qquad K_3 = ?$$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2} \tag{4.7.9}$$

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,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3 \tag{4.7.10}$$

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:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^{9}) = 1.3 \times 10^{-15} \tag{4.7.11}$$

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.

> *To determine K for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.*

✓ Example 4.7.2

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. $CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)}$ $\quad K_2 = 3.3 \times 10^4$

Calculate the equilibrium constant for the following reaction at the same temperature.

3. $CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)}$ $\quad K_3 = ?$

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:

$$CO_{(g)} + 3\cancel{H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 3\cancel{H_{2(g)}} + H_{2(g)}$$

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)}$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1 K_2 = (9.17 \times 10^{-2})(3.3 \times 10^4) = 3.03 \times 10^3$$

Exercise 4.7.2

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. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$ $\quad K_1 = 4.4 \times 10^{53}$
2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ $\quad K_2 = 2.6 \times 10^{12}$
3. $\frac{1}{8}S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ $\quad K_3 = ?$

Answer

$K_3 = 1.1 \times 10^{66}$

Summary

When a reaction is written in the reverse direction, K and the equilibrium constant expression are inverted. When the coefficients of an equilibrium reaction are changed, the equilibrium constant expression and magnitude will change accordingly. 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

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4.E: Fundamental Equilibrium Concepts (Exercises)

Template:HideTOC

4.E.1: 13.1: Chemical Equilibria Exercises

4.E.1.1: Q13.1.1

What does it mean to describe a reaction as “reversible”?

4.E.1.2: S13.1.1

The reaction can proceed in both the forward and reverse directions.

4.E.1.3: Q13.1.2

When writing an equation, how is a reversible reaction distinguished from a nonreversible reaction?

4.E.1.4: Q13.1.3

If a reaction is reversible, when can it be said to have reached equilibrium?

4.E.1.5: S13.1.3

When a system has reached equilibrium, no further changes in the reactant and product concentrations occur; the reactions continue to occur, but at equivalent rates.

4.E.1.6: Q13.1.4

Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?

4.E.1.7: Q13.1.5

If the concentrations of products and reactants are equal, is the system at equilibrium?

4.E.1.8: S13.1.5

The concept of equilibrium does not imply equal concentrations, though it is possible.

4.E.2: 13.2: Equilibrium Constant Exercises

4.E.2.1: Q13.2.1

Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

4.E.2.2: Q13.2.2

Explain why an equilibrium between $Br_2(l)$ and $Br_2(g)$ would not be established if the container were not a closed vessel shown below:

4.E.2.3: S13.2.2

Equilibrium cannot be established between the liquid and the gas phase if the top is removed from the bottle because the system is not closed; one of the components of the equilibrium, the Br_2 vapor, would escape from the bottle until all liquid disappeared. Thus, more liquid would evaporate than can condense back from the gas phase to the liquid phase.

4.E.2.4: Q13.2.3

If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4?

\[\ce{2NO2}(g) \rightleftharpoons \ce{N2O4}(g)\]

4.E.2.5: Q13.2.4

Among the solubility rules previously discussed is the statement: All chlorides are soluble except Hg_2Cl_2, AgCl, $PbCl_2$, and CuCl.

4.E.2.6: Q13.2.5

1. (a) Write the expression for the equilibrium constant for the reaction represented by the equation $\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{Cl}^{-}(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
2. (b) Write the expression for the equilibrium constant for the reaction represented by the equation $\mathrm{Pb}^{2+}(aq) + 2\,\mathrm{Cl}^{-}(aq) \rightleftharpoons \mathrm{PbCl}_2(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

4.E.2.7: S13.2.5

(a) $K_c = [\mathrm{Ag}^+][\mathrm{Cl}^-] < 1$. AgCl is insoluble; thus, the concentrations of ions are much less than 1 *M*; (b) $K_c = \dfrac{1}{[\mathrm{Pb}^{2+}][\mathrm{Cl}^-]^2} > 1$ because $PbCl_2$ is insoluble and formation of the solid will reduce the concentration of ions to a low level (<1 *M*).

4.E.2.8: Q13.2.6

Among the solubility rules previously discussed is the statement: Carbonates, phosphates, borates, and arsenates—except those of the ammonium ion and the alkali metals—are insoluble.

a. Write the expression for the equilibrium constant for the reaction represented by the equation $\mathrm{CaCO}_3(s) \rightleftharpoons \mathrm{Ca}^{2+}(aq) + \mathrm{CO}_3^{-}(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
b. Write the expression for the equilibrium constant for the reaction represented by the equation $3\,\mathrm{Ba}^{2+}(aq) + 2\,\mathrm{PO}_4^{3-}(aq) \rightleftharpoons \mathrm{Ba}_3(\mathrm{PO}_4)_2(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

4.E.2.9: Q13.2.7

Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3\,\mathrm{C}_2\mathrm{H}_2(g) \longrightarrow \mathrm{C}_6\mathrm{H}_6(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer.

4.E.2.10: S13.2.7

Since $K_c = \dfrac{[\mathrm{C}_6\mathrm{H}_6]}{[\mathrm{C}_2\mathrm{H}_2]^3}$, a value of $K_c \approx 10$ means that C_6H_6 predominates over C_2H_2. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

4.E.2.11: Q13.2.8

Show that the complete chemical equation, the total ionic equation, and the net ionic equation for the reaction represented by the equation $\mathrm{KI}(aq) + \mathrm{I}_2(aq) \rightleftharpoons \mathrm{KI}_3(aq)$ give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and I_3^-.

4.E.2.12: Q13.2.9

For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is $K_c > 1$, < 1, or ≈ 1 for a titration reaction?

4.E.2.13: S13.2.9

$K_c > 1$

4.E.2.14: Q13.2.10

For a precipitation reaction to be useful in a gravimetric analysis, the product of the reaction must be insoluble. Is $K_c > 1$, < 1, or ≈ 1 for a useful precipitation reaction?

4.E.2.15: Q13.2.11

Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

a. $\mathrm{CH_4}(g) + \mathrm{Cl_2}(g) \rightleftharpoons \mathrm{CH_3Cl}(g) + \mathrm{HCl}(g)$
b. $\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{NO}(g)$
c. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g)$
d. $\mathrm{BaSO_3}(s) \rightleftharpoons \mathrm{BaO}(s) + \mathrm{SO_2}(g)$
e. $\mathrm{P_4}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons \mathrm{P_4O_{10}}(s)$
f. $\mathrm{Br_2}(g) \rightleftharpoons 2\,\mathrm{Br}(g)$
g. $\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \rightleftharpoons \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$
h. $\mathrm{CuSO_4} \cdot 5\,\mathrm{H_2O}(s) \rightleftharpoons \mathrm{CuSO_4}(s) + 5\,\mathrm{H_2O}(g)$

4.E.2.16: S13.2.11

(a) $Q_c = \dfrac{[\mathrm{CH_3Cl}][\mathrm{HCl}]}{[\mathrm{CH_4}][\mathrm{Cl_2}]}$; (b) $Q_c = \dfrac{[\mathrm{NO}]^2}{[\mathrm{N_2}][\mathrm{O_2}]}$; (c) $Q_c = \dfrac{[\mathrm{SO_3}]^2}{[\mathrm{SO_2}]^2[\mathrm{O_2}]}$; (d) Q_c = [$\mathrm{SO_2}$]; (e) $Q_c = \dfrac{1}{[\mathrm{P_4}][\mathrm{O_2}]^5}$; (f) $Q_c = \dfrac{[\mathrm{Br}]^2}{[\mathrm{Br_2}]}$; (g) $Q_c = \dfrac{[\mathrm{CO_2}]}{[\mathrm{CH_4}][\mathrm{O_2}]^2}$; (h) Q_c = $[\mathrm{H_2O}]^5$

4.E.2.17: Q13.2.12

Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

a. $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g)$
b. $4\,\mathrm{NH_3}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons 4\,\mathrm{NO}(g) + 6\,\mathrm{H_2O}(g)$
c. $\mathrm{N_2O_4}(g) \rightleftharpoons 2\,\mathrm{NO_2}(g)$
d. $\mathrm{CO_2}(g) + \mathrm{H_2}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{H_2O}(g)$
e. $\mathrm{NH_4Cl}(s) \rightleftharpoons \mathrm{NH_3}(g) + \mathrm{HCl}(g)$
f. $2\,\mathrm{Pb(NO_3)_2}(s) \rightleftharpoons 2\,\mathrm{PbO}(s) + 4\,\mathrm{NO_2}(g) + \mathrm{O_2}(g)$
g. $2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{H_2O}(l)$
h. $\mathrm{S_8}(g) \rightleftharpoons 8\,\mathrm{S}(g)$

4.E.2.18: S13.2.12

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

a. $2\,\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \quad K_c = 17$; [$\mathrm{NH_3}$] = 0.20 *M*, [$\mathrm{N_2}$] = 1.00 *M*, [$\mathrm{H_2}$] = 1.00 *M*
b. $2\,\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \quad K_P = 6.8 \times 10^4$; initial pressures: $\mathrm{NH_3}$ = 3.0 atm, $\mathrm{N_2}$ = 2.0 atm, $\mathrm{H_2}$ = 1.0 atm
c. $2\,\mathrm{SO_3}(g) \rightleftharpoons 2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \quad K_c = 0.230$; [$\mathrm{SO_3}$] = 0.00 *M*, [$\mathrm{SO_2}$] = 1.00 *M*, [$\mathrm{O_2}$] = 1.00 *M*
d. $2\,\mathrm{SO_3}(g) \rightleftharpoons 2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \quad K_P = 16.5$; initial pressures: $\mathrm{SO_3}$ = 1.00 atm, $\mathrm{SO_2}$ = 1.00 atm, $\mathrm{O_2}$ = 1.00 atm
e. $2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{NOCl}(g) \quad K_c = 4.6 \times 10^4$; [NO] = 1.00 *M*, [$\mathrm{Cl_2}$] = 1.00 *M*, [NOCl] = 0 *M*
f. $\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{NO}(g) \quad K_P = 0.050$; initial pressures: NO = 10.0 atm, $\mathrm{N_2}$ = $\mathrm{O_2}$ = 5 atm

4.E.2.19: S13.2.13

(a) Q_c 25 proceeds left; (b) Q_P 0.22 proceeds right; (c) Q_c undefined proceeds left; (d) Q_P 1.00 proceeds right; (e) Q_P 0 proceeds right; (f) Q_c 4 proceeds left

4.E.2.20: Q13.2.14

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

a. $2\,\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \quad K_c = 17$; [$\mathrm{NH_3}$] = 0.50 *M*, [$\mathrm{N_2}$] = 0.15 *M*, [$\mathrm{H_2}$] = 0.12 *M*
b. $2\,\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \quad K_P = 6.8 \times 10^4$; initial pressures: $\mathrm{NH_3}$ = 2.00 atm, $\mathrm{N_2}$ = 10.00 atm, $\mathrm{H_2}$ = 10.00 atm
c. $2\,\mathrm{SO_3}(g) \rightleftharpoons 2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \quad K_c = 0.230$; [$\mathrm{SO_3}$] = 2.00 *M*, [$\mathrm{SO_2}$] = 2.00 *M*, [$\mathrm{O_2}$] = 2.00 *M*
d. $2\,\mathrm{SO_3}(g) \rightleftharpoons 2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \quad K_P = 6.5\ \mathrm{atm}$; initial pressures: $\mathrm{SO_2}$ = 1.00 atm, $\mathrm{O_2}$ = 1.130 atm, $\mathrm{SO_3}$ = 0 atm
e. $2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{NOCl}(g) \quad K_P = 2.5 \times 10^3$; initial pressures: NO = 1.00 atm, $\mathrm{Cl_2}$ = 1.00 atm, NOCl = 0 atm

f. $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \quad K_c = 0.050$; [N_2] = 0.100 *M*, [O_2] = 0.200 *M*, [NO] = 1.00 *M*

4.E.2.21: Q13.2.15

The following reaction has $K_P = 4.50 \times 10^{-5}$ at 720 K.

\[\ce{N2}(g)+\ce{3H2}(g) \rightleftharpoons \ce{2NH3}(g)\]

If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium? $P(NH_3)$ = 93 atm, $P(N_2)$ = 48 atm, and $P(H_2)$ = 52

4.E.2.22: S13.2.15

The system will shift toward the reactants to reach equilibrium.

4.E.2.23: Q13.2.16

Determine if the following system is at equilibrium. If not, in which direction will the system need to shift to reach equilibrium?

\(\ce{SO2Cl2}(g) \rightleftharpoons \ce{SO2}(g)+\ce{Cl2}(g)\)

[SO_2Cl_2] = 0.12 *M*, [Cl_2] = 0.16 *M* and [SO_2] = 0.050 *M*. K_c for the reaction is 0.078.

4.E.2.24: Q13.2.17

Which of the systems described in Exercise give homogeneous equilibria? Which give heterogeneous equilibria?

4.E.2.25: S13.2.17

(a) homogenous; (b) homogenous; (c) homogenous; (d) heterogeneous; (e) heterogeneous; (f) homogenous; (g) heterogeneous; (h) heterogeneous

4.E.2.26: Q13.2.18

Which of the systems described in Exercise give homogeneous equilibria? Which give heterogeneous equilibria?

4.E.2.27: Q13.2.19

For which of the reactions in Exercise does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

4.E.2.28: S13.2.19

This situation occurs in (a) and (b).

4.E.2.29: Q13.2.19

For which of the reactions in Exercise does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

4.E.2.30: Q13.2.20

Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

a. $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \quad K_c = 0.50 \text{ at } 400^\circ C$
b. $H_2 + I_2 \rightleftharpoons 2\,HI \quad K_c = 50.2 \text{ at } 448^\circ C$
c. $Na_2SO_4 \cdot 10\,H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10\,H_2O(g) \quad K_P = 4.08 \times 10^{-25} \text{ at } 25^\circ C$
d. $H_2O(l) \rightleftharpoons H_2O(g) \quad K_P = 0.122 \text{ at } 50^\circ C$

4.E.2.31: S13.2.20

(a) $K_P = 1.6 \times 10^{-4}$; (b) $K_P = 50.2$; (c) $K_c = 5.31 \times 10^{-39}$; (d) $K_c = 4.60 \times 10^{-3}$

4.E.2.32: Q13.2.21

Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

a. $Cl_2(g) + Br_2(g) \rightleftharpoons 2\,BrCl(g) \quad K_c = 4.7 \times 10^{-2} \text{ at } 25^\circ C$
b. $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \quad K_P = 48.2 \text{ at } 500^\circ C$
c. $CaCl_2 \cdot 6\,H_2O(s) \rightleftharpoons CaCl_2(s) + 6\,H_2O(g) \quad K_P = 5.09 \times 10^{-44} \text{ at } 25^\circ C$
d. $H_2O(l) \rightleftharpoons H_2O(g) \quad K_P = 0.196 \text{ at } 60^\circ C$

4.E.2.33: Q13.2.22

What is the value of the equilibrium constant expression for the change $H_2O(l) \rightleftharpoons H_2O(g)$ at 30 °C?

4.E.2.34: S13.2.22

$$K_P = P_{H_2O} = 0.042. \tag{4.E.1}$$

4.E.2.35: Q13.2.23

Write the expression of the reaction quotient for the ionization of HOCN in water.

4.E.2.36: Q13.2.24

Write the reaction quotient expression for the ionization of NH_3 in water.

4.E.2.37: S13.2.24

$$Q_c = \frac{[NH_4^+][OH^-]}{[HN_3]} \tag{4.E.2}$$

4.E.2.38: Q13.2.25

What is the approximate value of the equilibrium constant K_P for the change $C_2H_5OC_2H_5(l) \rightleftharpoons C_2H_5OC_2H_5(g)$ at 25 °C. (Vapor pressure was described in the previous chapter on liquids and solids; refer back to this chapter to find the relevant information needed to solve this problem.)

4.E.3: 13.3: Shifting Equilbria Exercises

4.E.3.1: Q13.3.1

The following equation represents a reversible decomposition:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Under what conditions will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains?

4.E.3.2: S13.3.1

The amount of $CaCO_3$ must be so small that P_{CO_2} is less than K_P when the $CaCO_3$ has completely decomposed. In other words, the starting amount of $CaCO_3$ cannot completely generate the full P_{CO_2} required for equilibrium.

4.E.3.3: Q13.3.2

Explain how to recognize the conditions under which changes in pressure would affect systems at equilibrium.

4.E.3.4: Q13.3.3

What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

4.E.3.5: S13.3.3

The change in enthalpy may be used. If the reaction is exothermic, the heat produced can be thought of as a product. If the reaction is endothermic the heat added can be thought of as a reactant. Additional heat would shift an exothermic reaction back to the reactants but would shift an endothermic reaction to the products. Cooling an exothermic reaction causes the reaction to shift toward the product side; cooling an endothermic reaction would cause it to shift to the reactants' side.

4.E.3.6: Q13.3.4

What would happen to the color of the solution in part (b) of Figure if a small amount of NaOH were added and Fe(OH)3 precipitated? Explain your answer.

4.E.3.7: Q13.3.5

The following reaction occurs when a burner on a gas stove is lit:

\(\ce{CH4}(g)+\ce{2O2}(g)\rightleftharpoons\ce{CO2}(g)+\ce{2H2O}(g)\)

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer.

4.E.3.8: S13.3.5

No, it is not at equilibrium. Because the system is not confined, products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

4.E.3.9: Q13.3.6

A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide, SO3, from sulfur dioxide, SO2, and oxygen, O2, shown here. At high temperatures, the rate of formation of SO_3 is higher, but the equilibrium amount (concentration or partial pressure) of SO3 is lower than it would be at lower temperatures.

$$2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g) \tag{4.E.3}$$

a. (a) Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?
b. (b) Is the reaction endothermic or exothermic?

4.E.3.10: Q13.3.7a

Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the following equation:

\[\ce{N2}(g)+\ce{2H2}(g)\rightleftharpoons\ce{N2H4}(g) \hspace{20px} ΔH=\ce{95\:kJ}\]

4.E.3.11: S13.3.7a

Add N_2; add H_2; decrease the container volume; heat the mixture.

4.E.3.12: Q13.3.7b

Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:

$$P_4(g) + 6\,H_2(g) \rightleftharpoons 4\,PH_3(g) \quad \Delta H = 110.5\text{ kJ} \tag{4.E.4}$$

4.E.3.13: Q13.3.8

How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

a. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \quad \Delta H = 92\text{ kJ}$
b. $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \quad \Delta H = 181\text{ kJ}$
c. $2\,O_3(g) \rightleftharpoons 3\,O_2(g) \quad \Delta H = -285\text{ kJ}$
d. $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \quad \Delta H = -176\text{ kJ}$

4.E.3.14: S13.3.8

(a) ΔT increase = shift right, ΔP increase = shift left; (b) ΔT increase = shift right, ΔP increase = no effect; (c) ΔT increase = shift left, ΔP increase = shift left; (d) ΔT increase = shift left, ΔP increase = shift right.

4.E.3.15: Q13.3.9

How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

a. $2\,H_2O(g) \rightleftharpoons 2\,H_2(g) + O_2(g) \quad \Delta H = 484\text{ kJ}$
b. $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \quad \Delta H = -92.2\text{ kJ}$
c. $2\,Br(g) \rightleftharpoons Br_2(g) \quad \Delta H = -224\text{ kJ}$
d. $H_2(g) + I_2(s) \rightleftharpoons 2\,HI(g) \quad \Delta H = 53\text{ kJ}$

4.E.3.16: Q13.3.10

Water gas is a 1:1 mixture of carbon monoxide and hydrogen gas and is called water gas because it is formed from steam and hot carbon in the following reaction:

$$H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g). \tag{4.E.5}$$

Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

a. Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$2\,\mathrm{H_2}(g)+\mathrm{CO}(g)\rightleftharpoons\mathrm{CH_3OH}(g)\quad \Delta H=-90.2\ \mathrm{kJ} \tag{4.E.6}$$

b. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?
c. What will happen to the concentrations of HH_2, CO, and CH_3OH at equilibrium if CO is removed?
d. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?
e. What will happen to the concentrations of HH_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased?
f. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more catalyst is added?

4.E.3.17: S13.3.10

a. $K_c=\dfrac{[\mathrm{CH_3OH}]}{[\mathrm{H_2}]^2[\mathrm{CO}]}$;
b. $[H_2]$ increases, [CO] decreases, $[CH_3OH]$ increases;
c. $[H_2]$ increases, [CO] decreases, $[CH_3OH]$ decreases;
d. $[H_2]$ increases, [CO] increases, $[CH_3OH]$ increases;
e. $[H_2]$ increases, [CO] increases, $[CH_3OH]$ decreases;
f. no changes.

4.E.3.18: Q13.3.11

Nitrogen and oxygen react at high temperatures.

a. Write the expression for the equilibrium constant (Kc) for the reversible reaction

$$\mathrm{N_2}(g)+\mathrm{O_2}(g)\rightleftharpoons 2\,\mathrm{NO}(g)\quad \Delta H=181\ \mathrm{kJ} \tag{4.E.7}$$

b. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if more O_2 is added?
c. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if N_2 is removed?
d. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if NO is added?
e. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?
f. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the temperature of the system is increased?
g. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if a catalyst is added?

4.E.3.19: Q13.3.12

Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.

a. Write the expression for the equilibrium constant for the reversible reaction

$$\mathrm{C}(s)+\mathrm{H_2O}(g)\rightleftharpoons\mathrm{CO}(g)+\mathrm{H_2}(g)\quad \Delta H=131.30\ \mathrm{kJ} \tag{4.E.8}$$

b. What will happen to the concentration of each reactant and product at equilibrium if more C is added?
c. What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?
d. What will happen to the concentration of each reactant and product at equilibrium if CO is added?
e. What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

4.E.3.20: S13.3.12

(a) $K_c=\dfrac{[\mathrm{CO}][\mathrm{H_2}]}{[\mathrm{H_2O}]}$; (b) $[H_2O]$ no change, [CO] no change, $[H_2]$ no change; (c) $[H_2O]$ decreases, [CO] decreases, $[H_2]$ decreases; (d) $[H_2O]$ increases, [CO] increases, $[H_2]$ decreases; (f) $[H_2O]$ decreases, [CO] increases, $[H_2]$ increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.

4.E.3.21: Q13.3.13

Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.

a. Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$\mathrm{Fe_2O_3}(s) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{Fe}(s) + 3\,\mathrm{H_2O}(g) \quad \Delta H = 98.7\ \mathrm{kJ} \tag{4.E.9}$$

b. What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?
c. What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?
d. What will happen to the concentration of each reactant and product at equilibrium if H_2 is added?
e. What will happen to the concentration of each reactant and product at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?
f. What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

4.E.3.22: Q13.3.14

Ammonia is a weak base that reacts with water according to this equation:

\[\ce{NH3}(aq)+\ce{H2O}(l)\rightleftharpoons\ce{NH4+}(aq)+\ce{OH-}(aq)\]

Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water and why?

a. Addition of NaOH
b. Addition of HCl
c. Addition of NH_4Cl

4.E.3.23: S13.3.14

Only (b)

4.E.3.24: Q13.3.15

Acetic acid is a weak acid that reacts with water according to this equation:

\[\ce{CH3CO2H}(aq)+\ce{H2O}(aq)\rightleftharpoons\ce{H3O+}(aq)+\ce{CH3CO2-}(aq)\]

Will any of the following increase the percent of acetic acid that reacts and produces $\mathrm{CH_3CO_2^-}$ ion?

a. Addition of HCl
b. Addition of NaOH
c. Addition of $NaCH_3CO_2$

4.E.3.25: Q13.3.16

Suggest two ways in which the equilibrium concentration of Ag+ can be reduced in a solution of Na^+, Cl^-, Ag^+, and $\mathrm{NO_3^-}$, in contact with solid AgCl.

\(\ce{Na+}(aq)+\ce{Cl-}(aq)+\ce{Ag+}(aq)+\ce{NO3-}(aq)\rightleftharpoons\ce{AgCl}(s)+\ce{Na+}(aq)+\ce{NO3-}(aq)\)

$$\Delta H = -65.9\ \mathrm{kJ}$$

4.E.3.26: S13.3.16

Add NaCl or some other salt that produces Cl− to the solution. Cooling the solution forces the equilibrium to the right, precipitating more AgCl(s).

4.E.3.27: Q13.3.17

How can the pressure of water vapor be increased in the following equilibrium?

\[\ce{H2O}(l)\rightleftharpoons\ce{H2O}(g) \hspace{20px} ΔH=\ce{41\:kJ}\]

4.E.3.28: Q13.3.18

Additional solid silver sulfate, a slightly soluble solid, is added to a solution of silver ion and sulfate ion at equilibrium with solid silver sulfate.

\[\ce{2Ag+}(aq)+\ce{SO4^2-}(aq)\rightleftharpoons\ce{Ag2SO4}(s)\]

Which of the following will occur?

a. Ag^+ or $\mathrm{SO_4^{2-}}$ concentrations will not change.
b. The added silver sulfate will dissolve.

c. Additional silver sulfate will form and precipitate from solution as Ag^+ ions and SO_4^{2-} ions combine.
d. The Ag^+ ion concentration will increase and the SO_4^{2-} ion concentration will decrease.

4.E.3.29: S13.3.18

(a)

4.E.3.30: Q13.3.19

The amino acid alanine has two isomers, α-alanine and β-alanine. When equal masses of these two compounds are dissolved in equal amounts of a solvent, the solution of α-alanine freezes at the lowest temperature. Which form, α-alanine or β-alanine, has the larger equilibrium constant for ionization $(\mathrm{HX} \rightleftharpoons \mathrm{H^+} + \mathrm{X^-})$?

4.E.4: 13.4: Equilibrium Calculations Exercises

4.E.4.1: Q13.4.1

A reaction is represented by this equation: $\mathrm{A}(aq) + 2\,\mathrm{B}(aq) \rightleftharpoons 2\,\mathrm{C}(aq) \quad K_c = 1 \times 10^3$

a. Write the mathematical expression for the equilibrium constant.
b. Using concentrations ≤1 *M*, make up two sets of concentrations that describe a mixture of A, B, and C at equilibrium.

4.E.4.2: S13.4.1

$K_c = \dfrac{[\mathrm{C}]^2}{[\mathrm{A}][\mathrm{B}]^2}$. [A] = 0.1 *M*, [B] = 0.1 *M*, [C] = 1 *M*; and [A] = 0.01, [B] = 0.250, [C] = 0.791.

4.E.4.3: Q13.4.2

A reaction is represented by this equation: $2\,\mathrm{W}(aq) \rightleftharpoons \mathrm{X}(aq) + 2\,\mathrm{Y}(aq) \quad K_c = 5 \times 10^{-4}$

a. Write the mathematical expression for the equilibrium constant.
b. Using concentrations of ≤1 *M*, make up two sets of concentrations that describe a mixture of W, X, and Y at equilibrium.

4.E.4.4: Q13.4.3

What is the value of the equilibrium constant at 500 °C for the formation of NH_3 according to the following equation?

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \tag{4.E.10}$$

An equilibrium mixture of $NH_3(g)$, $H_2(g)$, and $N_2(g)$ at 500 °C was found to contain 1.35 *M* H_2, 1.15 *M* N_2, and 4.12×10^{-1} *M* NH_3.

4.E.4.5: S13.4.3

$K_c = 6.00 \times 10^{-2}$

4.E.4.6: Q13.4.4

Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.

$$\mathrm{CH_4}(g) + \mathrm{H_2O}(g) \rightleftharpoons 3\,\mathrm{H_2}(g) + \mathrm{CO}(g) \tag{4.E.11}$$

What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 *M*; H_2O, 0.242 *M*; CO, 0.126 *M*; H_2 1.15 *M*, at a temperature of 760 °C?

A 0.72-mol sample of PCl_5 is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of $PCl_3(g)$ and 0.40 mol of $Cl_2(g)$. Calculate the value of the equilibrium constant for the decomposition of PCl_5 to PCl_3 and Cl_2 at this temperature.

4.E.4.7: S13.4.4

$K_c = 0.50$

4.E.4.8: Q13.4.5

At 1 atm and 25 °C, NO_2 with an initial concentration of 1.00 *M* is 3.3×10^{-3}% decomposed into NO and O_2. Calculate the value of the equilibrium constant for the reaction.

$$2\,\mathrm{NO_2}(g) \rightleftharpoons 2\,\mathrm{NO}(g) + \mathrm{O_2}(g) \tag{4.E.12}$$

4.E.4.9: Q13.4.6

Calculate the value of the equilibrium constant K_P for the reaction $2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{NOCl}(g)$ from these equilibrium pressures: NO, 0.050 atm; Cl_2, 0.30 atm; NOCl, 1.2 atm.

4.E.4.10: S13.4.6

The equilibrium equation is $K_P = 1.9 \times 10^3$

4.E.4.11: Q13.4.7

When heated, iodine vapor dissociates according to this equation:

$$\mathrm{I_2}(g) \rightleftharpoons 2\,\mathrm{I}(g) \tag{4.E.13}$$

At 1274 K, a sample exhibits a partial pressure of I_2 of 0.1122 atm and a partial pressure due to I atoms of 0.1378 atm. Determine the value of the equilibrium constant, K_P, for the decomposition at 1274 K.

4.E.4.12: Q13.4.8

A sample of ammonium chloride was heated in a closed container.

$$\mathrm{NH_4Cl}(s) \rightleftharpoons \mathrm{NH_3}(g) + \mathrm{HCl}(g) \tag{4.E.14}$$

At equilibrium, the pressure of $NH_3(g)$ was found to be 1.75 atm. What is the value of the equilibrium constant K_P for the decomposition at this temperature?

4.E.4.13: S13.4.8

$K_P = 3.06$

4.E.4.14: Q13.4.9

At a temperature of 60 °C, the vapor pressure of water is 0.196 atm. What is the value of the equilibrium constant K_P for the transformation at 60 °C?

$$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g) \tag{4.E.15}$$

4.E.4.15: Q13.4.10

Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

(a)

$$2\,\mathrm{SO_3}(g) \rightleftharpoons 2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \tag{4.E.16}$$

$$\_\_\_\_\_ \qquad \_\_\_\_\_ \qquad +x \tag{4.E.17}$$

$$\_\_\_\_\_ \qquad \_\_\_\_\_ \qquad 0.125\ M \tag{4.E.18}$$

(b)

$$4\,\mathrm{NH_3}(g) + 3\,\mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{N_2}(g) + 6\,\mathrm{H_2O}(g) \tag{4.E.19}$$

$$\_\_\_\_\_ \qquad 3x \qquad \_\_\_\_\_ \qquad \_\_\_\_\_ \tag{4.E.20}$$

$$\_\_\_\_\_ \qquad 0.24\ M \qquad \_\_\_\_\_ \qquad \_\_\_\_\_ \tag{4.E.21}$$

(c) Change in pressure:

$$2\,\mathrm{CH_4}(g) \rightleftharpoons \mathrm{C_2H_2}(g) + 3\,\mathrm{H_2}(g) \tag{4.E.22}$$

$$\_\_\_\_\_ \qquad x \qquad \_\_\_\_\_ \tag{4.E.23}$$

$$\_\_\_\_\_ \qquad 25\ \mathrm{torr} \qquad \_\_\_\_\_ \tag{4.E.24}$$

(d) Change in pressure:

$$\mathrm{CH_4}(g) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO}(g) + 3\,\mathrm{H_2}(g) \tag{4.E.25}$$

$$\_\_\_\_\_ \qquad x \qquad \_\_\_\_\_ \qquad \_\_\_\_\_ \tag{4.E.26}$$

$$\_\_\_\_\_ \qquad 5\ \mathrm{atm} \qquad \_\_\_\_\_ \qquad \_\_\_\_\_ \tag{4.E.27}$$

(e)

$$\mathrm{NH_4Cl}(s) \rightleftharpoons \mathrm{NH_3}(g) + \quad \mathrm{HCl}(g) \tag{4.E.28}$$

$$x \qquad \_\_\_\_\_ \tag{4.E.29}$$

$$1.03\times10^{-4}\ M \_\_\_\_\_ \tag{4.E.30}$$

(f) change in pressure:

$$\mathrm{Ni}(s) + 4\,\mathrm{CO}(g) \rightleftharpoons \mathrm{Ni(CO)_4}(g) \tag{4.E.31}$$

$$4x \qquad \_\_\_\_\_ \tag{4.E.32}$$

$$0.40\ \mathrm{atm} \qquad \_\_\_\_\_ \tag{4.E.33}$$

4.E.4.16: S13.4.10

a. −2*x*, 2*x*, −0.250 *M*, 0.250 *M*;
b. 4*x*, −2*x*, −6*x*, 0.32 *M*, −0.16 *M*, −0.48 *M*;
c. −2*x*, 3*x*, −50 torr, 75 torr;
d. *x*, − *x*, −3*x*, 5 atm, −5 atm, −15 atm;
e. *x*, 1.03×10^{-4} *M*; (f) *x*, 0.1 atm.

4.E.4.17: Q13.4.11

Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

(a)

$$2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{H_2O}(g) \tag{4.E.34}$$

$$\_\_\_\_\_ \qquad \_\_\_\_\_ \qquad +2x \tag{4.E.35}$$

$$\_\_\_\_\_ \qquad \_\_\_\_\_ \qquad 1.50\ M \tag{4.E.36}$$

(b)

$$\mathrm{CS_2}(g) + 4\,\mathrm{H_2}(g) \rightleftharpoons \mathrm{CH_4}(g) + 2\,\mathrm{H_2S}(g) \tag{4.E.37}$$

$$x \quad \_\_\_\_\_ \qquad \_\_\_\_\_ \qquad \_\_\_\_\_ \tag{4.E.38}$$

$$0.020\ M \quad \_\_\_\_\_ \qquad \_\_\_\_\_ \qquad \_\_\_\_\_ \tag{4.E.39}$$

(c) Change in pressure:

$$\mathrm{H_2}(g) + \ \mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{HCl}(g) \tag{4.E.40}$$

$$x \qquad \_\_\_\_\_ \qquad \_\_\_\_\_ \tag{4.E.41}$$

$$1.50\ \mathrm{atm}\_\_\_\_\_ \qquad \_\_\_\_\_ \tag{4.E.42}$$

(d) Change in pressure:

$$2\,\mathrm{NH_3}(g) + 2\,\mathrm{O_2}(g) \rightleftharpoons \mathrm{N_2O}(g) + 3\,\mathrm{H_2O}(g) \tag{4.E.43}$$

$$\_\_\_\_\_ \qquad \_\_\_\_\_ \qquad \_\_\_\_\_ \qquad x \tag{4.E.44}$$

$$\_\_\_\_\_ \qquad \_\_\_\_\_ \qquad \_\_\_\_\_ \qquad 60.6\ \mathrm{torr} \tag{4.E.45}$$

(e)

$$\mathrm{NH_4HS}(s) \rightleftharpoons \mathrm{NH_3}(g) + \quad \mathrm{H_2S}(g) \tag{4.E.46}$$

$$x \qquad \_\_\_\_\_ \tag{4.E.47}$$

$$9.8\times10^{-6}\ M\_\_\_\_\_ \tag{4.E.48}$$

(f) Change in pressure:

$$\mathrm{Fe}(s) + 5\,\mathrm{CO}(g) \rightleftharpoons \mathrm{Fe(CO)_4}(g) \tag{4.E.49}$$

$$\_\_\_\_\_ \qquad x \tag{4.E.50}$$

$$\_\_\_\_\_ \qquad 0.012\ \mathrm{atm} \tag{4.E.51}$$

4.E.4.18: Q13.4.12

Why are there no changes specified for Ni in Exercise, part (f)? What property of Ni does change?

4.E.4.19: S13.4.12

Activities of pure crystalline solids equal 1 and are constant; however, the mass of Ni does change.

4.E.4.20: Q13.4.13

Why are there no changes specified for NH_4HS in Exercise, part (e)? What property of NH_4HS does change?

4.E.4.21: Q13.4.14

Analysis of the gases in a sealed reaction vessel containing NH_3, N_2, and H_2 at equilibrium at 400 °C established the concentration of N_2 to be 1.2 *M* and the concentration of H_2 to be 0.24 *M*.

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \quad K_c = 0.50 \text{ at } 400\ {}^\circ\mathrm{C} \tag{4.E.52}$$

Calculate the equilibrium molar concentration of NH_3.

4.E.4.22: S13.4.14

$[NH_3] = 9.1 \times 10^{-2}\ M$

4.E.4.23: Q13.4.16

Calculate the number of moles of HI that are at equilibrium with 1.25 mol of H_2 and 1.25 mol of I_2 in a 5.00−L flask at 448 °C.

$$\mathrm{H_2} + \mathrm{I_2} \rightleftharpoons 2\,\mathrm{HI} \quad K_c = 50.2 \text{ at } 448\ {}^\circ\mathrm{C}$$

4.E.4.24: Q13.4.17

What is the pressure of BrCl in an equilibrium mixture of Cl_2, Br_2, and BrCl if the pressure of Cl_2 in the mixture is 0.115 atm and the pressure of Br_2 in the mixture is 0.450 atm?

$$\mathrm{Cl_2}(g) + \mathrm{Br_2}(g) \rightleftharpoons 2\,\mathrm{BrCl}(g) \quad K_P = 4.7 \times 10^{-2} \tag{4.E.53}$$

4.E.4.25: S13.4.17

$P_{BrCl} = 4.9 \times 10^{-2}$ atm

4.E.4.26: Q13.4.18

What is the pressure of CO_2 in a mixture at equilibrium that contains 0.50 atm H_2, 2.0 atm of H_2O, and 1.0 atm of CO at 990 °C?

$$\mathrm{H_2}(g) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{H_2O}(g) + \mathrm{CO}(g) \quad K_P = 1.6 \text{ at } 990\ {}^\circ\mathrm{C} \tag{4.E.54}$$

4.E.4.27: Q13.4.12

Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.

$$\mathrm{CoO}(s) + \mathrm{CO}(g) \rightleftharpoons \mathrm{Co}(s) + \mathrm{CO_2}(g) \quad K_c = 4.90 \times 10^2 \text{ at } 550\ {}^\circ\mathrm{C}$$

What concentration of CO remains in an equilibrium mixture with $[CO_2] = 0.100\ M$?

4.E.4.28: S13.4.12

$[CO] = 2.0 \times 10^{-4}\ M$

4.E.4.29: Q13.4.13

Carbon reacts with water vapor at elevated temperatures.

$$\mathrm{C}(s) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{H_2}(g) \quad K_c = 0.2 \text{ at } 1000\ {}^\circ\mathrm{C}$$

What is the concentration of CO in an equilibrium mixture with $[H_2O] = 0.500\ M$ at 1000 °C?

4.E.4.30: Q13.4.14

Sodium sulfate 10−hydrate, $\mathrm{Na_2SO_4 \cdot 10\,H_2O}$, dehydrates according to the equation

$$\mathrm{Na_2SO_4 \cdot 10\,H_2O}(s) \rightleftharpoons \mathrm{Na_2SO_4}(s) + 10\,\mathrm{H_2O}(g) \tag{4.E.55}$$

with $K_p = 4.08 \times 10^{-25}$ at 25°C. What is the pressure of water vapor at equilibrium with a mixture of $\mathrm{Na_2SO_4 \cdot 10\,H_2O}$ and $\mathrm{NaSO_4}$?

4.E.4.31: S13.4.14

$P_{H_2O} = 3.64 \times 10^{-3}$ atm

4.E.4.32: Q13.4.15

Calcium chloride 6−hydrate, $CaCl_2 \cdot 6H_2O$, dehydrates according to the equation

$$CaCl_2 \cdot 6\,H_2O(s) \rightleftharpoons CaCl_2(s) + 6\,H_2O(g) \quad K_P = 5.09 \times 10^{-44} \text{ at } 25\ ^\circ C$$

What is the pressure of water vapor at equilibrium with a mixture of $CaCl_2 \cdot 6H_2O$ and $CaCl_2$?

4.E.4.33: Q13.4.16

A student solved the following problem and found the equilibrium concentrations to be $[SO_2]$ = 0.590 *M*, $[O_2]$ = 0.0450 *M*, and $[SO_3]$ = 0.260 *M*. How could this student check the work without reworking the problem? The problem was: For the following reaction at 600 °C:

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \quad K_c = 4.32$$

What are the equilibrium concentrations of all species in a mixture that was prepared with $[SO_3]$ = 0.500 *M*, $[SO_2]$ = 0 *M*, and $[O_2]$ = 0.350 *M*?

4.E.4.34: S13.4.16

Calculate *Q* based on the calculated concentrations and see if it is equal to K_c. Because *Q* does equal 4.32, the system must be at equilibrium.

4.E.4.35: Q13.4.16

A student solved the following problem and found $[N_2O_4]$ = 0.16 *M* at equilibrium. How could this student recognize that the answer was wrong without reworking the problem? The problem was: What is the equilibrium concentration of N_2O_4 in a mixture formed from a sample of NO_2 with a concentration of 0.10 *M*?

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g) \quad K_c = 160 \tag{4.E.56}$$

Assume that the change in concentration of N_2O_4 is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of both species in 1.00 L of a solution prepared from 0.129 mol of N_2O_4 with chloroform as the solvent.

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \quad K_c = 1.07 \times 10^{-5} \text{ in chloroform}$$

(b) Show that the change is small enough to be neglected.

4.E.4.36: S13.4.16

(a)

- $[NO_2]$ = 1.17×10^{-3} *M*
- $[N_2O_4]$ = 0.128 *M*

(b) Percent error $= \dfrac{5.87 \times 10^{-4}}{0.129} \times 100\% = 0.455\%$. The change in concentration of N_2O_4 is far less than the 5% maximum allowed.

4.E.4.37: Q13.4.17

Assume that the change in concentration of $COCl_2$ is small enough to be neglected in the following problem.

a. Calculate the equilibrium concentration of all species in an equilibrium mixture that results from the decomposition of $COCl_2$ with an initial concentration of 0.3166 *M*.

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g) \quad K_c = 2.2 \times 10^{-10} \tag{4.E.57}$$

b. Show that the change is small enough to be neglected.

4.E.4.38: Q13.4.18

Assume that the change in pressure of H_2S is small enough to be neglected in the following problem.

(a) Calculate the equilibrium pressures of all species in an equilibrium mixture that results from the decomposition of H_2S with an initial pressure of 0.824 atm.

$2\,\mathrm{H_2S}(g) \rightleftharpoons 2\,\mathrm{H_2}(g) + \mathrm{S_2}(g) \quad K_P = 2.2 \times 10^{-6}$

(b) Show that the change is small enough to be neglected.

4.E.4.39: S13.4.18

(a)

- $[H_2S]$ = 0.810 atm
- $[H_2]$ = 0.014 atm
- $S_2]$ = 0.0072 atm

(b) The 2*x* is dropped from the equilibrium calculation because 0.014 is negligible when subtracted from 0.824. The percent error associated with ignoring 2*x* is $\frac{0.014}{0.824} \times 100\% = 1.7\%$, which is less than allowed by the “5% test.” The error is, indeed, negligible.

4.E.4.40: Q13.4.19

What are all concentrations after a mixture that contains $[H_2O]$ = 1.00 *M* and $[Cl_2O]$ = 1.00 *M* comes to equilibrium at 25 °C?

$$\mathrm{H_2O}(g) + \mathrm{Cl_2O}(g) \rightleftharpoons 2\,\mathrm{HOCl}(g) \quad K_c = 0.0900 \tag{4.E.58}$$

4.E.4.41: Q13.4.20

What are the concentrations of PCl_5, PCl_3, and Cl_2 in an equilibrium mixture produced by the decomposition of a sample of pure PCl_5 with $[PCl_5]$ = 2.00 *M*?

$$\mathrm{PCl_5}(g) \rightleftharpoons \mathrm{PCl_3}(g) + \mathrm{Cl_2}(g) \quad K_c = 0.0211 \tag{4.E.59}$$

4.E.4.42: S13.4.20

$[PCl_3]$ = 1.80 *M*; $[PC_3]$ = 0.195 *M*; $[PCl_3]$ = 0.195 *M*.

4.E.4.43: Q13.4.21

Calculate the pressures of all species at equilibrium in a mixture of NOCl, NO, and Cl_2 produced when a sample of NOCl with a pressure of 10.0 atm comes to equilibrium according to this reaction:

$$2\,\mathrm{NOCl}(g) \rightleftharpoons 2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \quad K_P = 4.0 \times 10^{-4} \tag{4.E.60}$$

4.E.4.44: Q13.4.22

Calculate the equilibrium concentrations of NO, O_2, and NO_2 in a mixture at 250 °C that results from the reaction of 0.20 *M* NO and 0.10 *M* O_2. (Hint: *K* is large; assume the reaction goes to completion then comes back to equilibrium.)

$$2\,\mathrm{NO}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{NO_2}(g) \quad K_c = 2.3 \times 10^5 \text{ at } 250\ ^\circ\mathrm{C} \tag{4.E.61}$$

4.E.4.45: S13.4.22

- $[NO_2]$ = 0.19 *M*
- [NO] = 0.0070 *M*
- $[O_2]$ = 0.0035 *M*

4.E.4.46: Q13.4.23

Calculate the equilibrium concentrations that result when 0.25 *M* O_2 and 1.0 *M* HCl react and come to equilibrium.

$$4\,\mathrm{HCl}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{Cl_2}(g) + 2\,\mathrm{H_2O}(g) \quad K_c = 3.1 \times 10^{13} \tag{4.E.62}$$

4.E.4.47: Q13.4.24

One of the important reactions in the formation of smog is represented by the equation

$$O_3(g) + NO(g) \rightleftharpoons NO_2(g) + O_2(g) \quad K_P = 6.0 \times 10^{34} \tag{4.E.63}$$

What is the pressure of O_3 remaining after a mixture of O_3 with a pressure of 1.2 × 10^{-8} atm and NO with a pressure of 1.2 × 10^{-8} atm comes to equilibrium? (Hint: K_P is large; assume the reaction goes to completion then comes back to equilibrium.)

4.E.4.48: S13.4.24

$P_{O_3} = 4.9 \times 10^{-26}$ atm

4.E.4.49: Q13.4.24

Calculate the pressures of NO, Cl_2, and NOCl in an equilibrium mixture produced by the reaction of a starting mixture with 4.0 atm NO and 2.0 atm Cl_2. (Hint: K_P is small; assume the reverse reaction goes to completion then comes back to equilibrium.)

$$2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g) \quad K_P = 2.5 \times 10^3$$

4.E.4.50: Q13.4.25

Calculate the number of grams of HI that are at equilibrium with 1.25 mol of H_2 and 63.5 g of iodine at 448 °C.

$$H_2 + I_2 \rightleftharpoons 2\,HI \quad K_c = 50.2 \text{ at } 448\ ^\circ C$$

4.E.4.51: S13.4.25

507 g

4.E.4.52: Q13.4.26

Butane exists as two isomers, *n*−butane and isobutane.

Three Lewis structures are shown. The first is labeled, “n dash Butane,” and has a C H subscript 3 single bonded to a C H subscript 2 group. This C H subscript 2 group is single bonded to another C H subscript 2 group which is single bonded to a C H subscript 3 group. The second is labeled, “iso dash Butane,” and is composed of a C H group single bonded to three C H subscript 3 groups. The third structure shows a chain of atoms: “C H subscript 3, C H subscript 2, C H subscript 2, C H subscript 3,” a double-headed arrow, then a carbon atom single bonded to three C H subscript 3 groups as well as a hydrogen atom.

K_P = 2.5 at 25 °C

What is the pressure of isobutane in a container of the two isomers at equilibrium with a total pressure of 1.22 atm?

4.E.4.53: Q13.4.27

What is the minimum mass of $CaCO_3$ required to establish equilibrium at a certain temperature in a 6.50-L container if the equilibrium constant (K_c) is 0.050 for the decomposition reaction of $CaCO_3$ at that temperature?

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

4.E.4.54: S13.4.27

330 g

4.E.4.55: Q13.4.28

The equilibrium constant (K_c) for this reaction is 1.60 at 990 °C:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \tag{4.E.64}$$

Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of H_2, 2.00 mol of CO_2, 0.750 mol of H_2O, and 1.00 mol of CO to a 5.00-L container at 990 °C.

4.E.4.56: Q13.4.29

At 25 °C and at 1 atm, the partial pressures in an equilibrium mixture of N_2O_4 and NO_2 are $P_{N_2O_4} = 0.70$ atm and $P_{NO_2} = 0.30$ atm.

a. Predict how the pressures of NO_2 and N_2O_4 will change if the total pressure increases to 9.0 atm. Will they increase, decrease, or remain the same?
b. Calculate the partial pressures of NO_2 and N_2O_4 when they are at equilibrium at 9.0 atm and 25 °C.

4.E.4.57: S13.4.29

(a) Both gases must increase in pressure.

(b) $P_{N_2O_4} = 8.0 \text{ atm and } P_{NO_2} = 1.0 \text{ atm}$

4.E.4.58: Q13.4.30

In a 3.0-L vessel, the following equilibrium partial pressures are measured: N_2, 190 torr; H_2, 317 torr; NH_3, 1.00 × 10^3 torr.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \tag{4.E.65}$$

a. How will the partial pressures of H_2, N_2, and NH_3 change if H_2 is removed from the system? Will they increase, decrease, or remain the same?
b. Hydrogen is removed from the vessel until the partial pressure of nitrogen, at equilibrium, is 250 torr. Calculate the partial pressures of the other substances under the new conditions.

4.E.4.59: Q13.4.31

The equilibrium constant (K_c) for this reaction is 5.0 at a given temperature.

\[\ce{CO}(g)+\ce{H2O}(g) <=> \ce{CO2}(g)+\ce{H2}(g)\)]

a. On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of CO, 0.30 mol of water vapor, and 0.90 mol of H_2 in a liter. How many moles of CO_2 were there in the equilibrium mixture?
b. Maintaining the same temperature, additional H_2 was added to the system, and some water vapor was removed by drying. A new equilibrium mixture was thereby established containing 0.40 mol of CO, 0.30 mol of water vapor, and 1.2 mol of H_2 in a liter. How many moles of CO_2 were in the new equilibrium mixture? Compare this with the quantity in part (a), and discuss whether the second value is reasonable. Explain how it is possible for the water vapor concentration to be the same in the two equilibrium solutions even though some vapor was removed before the second equilibrium was established.

4.E.4.60: S13.4.31

(a) 0.33 mol.

(b) $[CO]^2$ = 0.50 *M* Added H_2 forms some water to compensate for the removal of water vapor and as a result of a shift to the left after H_2 is added.

4.E.4.61: Q13.4.32a

Antimony pentachloride decomposes according to this equation:

$$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$$

An equilibrium mixture in a 5.00-L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2. How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

4.E.4.62: Q13.4.32b

Consider the reaction between H_2 and O_2 at 1000 K

\[\ce{2H2}(g)+\ce{O2}(g)⇌\ce{2H2O}(g) \hspace{20px} K_P=\dfrac{(P_{\ce{H2O}})^2}{(P_{\ce{O2}})(P_{\ce{H2}})^3}=1.33×10^{20}\]

If 0.500 atm of H_2 and 0.500 atm of O_2 are allowed to come to equilibrium at this temperature, what are the partial pressures of the components?

4.E.4.63: S13.4.32b

$P_{H_2} = 8.64 \times 10^{-11} \text{ atm}$

\(P_{\ce{O2}}=0.250\:\ce{atm}\)

\(P_{\ce{H2O}}=0.500\:\ce{atm}\)

4.E.4.64: Q13.4.33

An equilibrium is established according to the following equation

$$\mathrm{Hg_2^{2+}}(aq) + \mathrm{NO_3}-(aq) + 3\,\mathrm{H^+}(aq) \rightleftharpoons 2\,\mathrm{Hg^{2+}}(aq) + \mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \quad K_c = 4.6 \tag{4.E.66}$$

What will happen in a solution that is 0.20 *M* each in $\mathrm{Hg_2^{2+}}$, $\mathrm{NO_3}-$, H^+, Hg^{2+}, and HNO_2?

a. $\mathrm{Hg_2^{2+}}$ will be oxidized and $\mathrm{NO_3}-$ reduced.
b. $\mathrm{Hg_2^{2+}}$ will be reduced and $\mathrm{NO_3}-$ oxidized.
c. Hg^{2+} will be oxidized and HNO_2 reduced.
d. Hg^{2+} will be reduced and HNO_2 oxidized.
e. There will be no change because all reactants and products have an activity of 1.

4.E.4.65: Q13.4.34

Consider the equilibrium

$$4\,\mathrm{NO_2}(g) + 6\,\mathrm{H_2O}(g) \rightleftharpoons 4\,\mathrm{NH_3}(g) + 7\,\mathrm{O_2}(g) \tag{4.E.67}$$

a. What is the expression for the equilibrium constant (K_c) of the reaction?
b. How must the concentration of NH_3 change to reach equilibrium if the reaction quotient is less than the equilibrium constant?
c. If the reaction were at equilibrium, how would a decrease in pressure (from an increase in the volume of the reaction vessel) affect the pressure of NO_2?
d. If the change in the pressure of NO_2 is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of O_2 change?

4.E.4.66: S13.4.34

(a) $K_c = \dfrac{[\mathrm{NH_3}]^4[\mathrm{O_2}]^7}{[\mathrm{NO_2}]^4[\mathrm{H_2O}]^6}$. (b) $[NH_3]$ must increase for Q_c to reach K_c. (c) That decrease in pressure would decrease $[NO_2]$. (d) $P_{\mathrm{O_2}} = 49$ torr

4.E.4.67: Q13.4.35

The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin (HbO_2), is partially regulated by the concentration of H_3O^+ and dissolved CO_2 in the blood. Although the equilibrium is complicated, it can be summarized as

$$\mathrm{HbO_2}(aq) + \mathrm{H_3O^+}(aq) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CO_2}-\mathrm{Hb}-\mathrm{H^+} + \mathrm{O_2}(g) + \mathrm{H_2O}(l)$$

1. (a) Write the equilibrium constant expression for this reaction.
2. (b) Explain why the production of lactic acid and CO_2 in a muscle during exertion stimulates release of O_2 from the oxyhemoglobin in the blood passing through the muscle.

4.E.4.68: Q13.4.36

The hydrolysis of the sugar sucrose to the sugars glucose and fructose follows a first-order rate equation for the disappearance of sucrose.

$$\mathrm{C_{12}H_{22}O_{11}}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{C_6H_{12}O_6}(aq) + \mathrm{C_6H_{12}O_6}(aq)$$

Rate = $k[\mathrm{C_{12}H_{22}O_{11}}]$

In neutral solution, $k = 2.1 \times 10^{-11}$/s at 27 °C. (As indicated by the rate constant, this is a very slow reaction. In the human body, the rate of this reaction is sped up by a type of catalyst called an enzyme.) (Note: That is not a mistake in the equation—the products of the reaction, glucose and fructose, have the same molecular formulas, $C_6H_{12}O_6$, but differ in the arrangement of the atoms in their molecules). The equilibrium constant for the reaction is 1.36×10^5 at 27 °C. What are the concentrations of glucose, fructose, and sucrose after a 0.150 *M* aqueous solution of sucrose has reached equilibrium? Remember that the activity of a solvent (the effective concentration) is 1.

4.E.4.69: S13.4.36

[fructose] = 0.15 *M*

4.E.4.70: Q13.4.37

The density of trifluoroacetic acid vapor was determined at 118.1 °C and 468.5 torr, and found to be 2.784 g/L. Calculate K_c for the association of the acid.

Two Lewis structures are shown in a reaction. The first structure, which is condensed, reads, "2 C F subscript 3 C O subscript 2 H (g)," and is followed by a double-headed arrow. The second structure shows a partially condensed hexagonal ring shape. From the left side, in a clockwise manner, it reads "C F subscript 3 C, single bond, O, single bond, H, dotted line bond, O, double bond, C F subscript 3 C (g), single bond, O, single bond, H, dotted line bond, O, double bond back to the starting compound."

Liquid N_2O_3 is dark blue at low temperatures, but the color fades and becomes greenish at higher temperatures as the compound decomposes to NO and NO_2. At 25 °C, a value of K_P = 1.91 has been established for this decomposition. If 0.236 moles of N_2O_3 are placed in a 1.52-L vessel at 25 °C, calculate the equilibrium partial pressures of $N_2O_3(g)$, $NO_2(g)$, and $NO(g)$.

4.E.4.71: S13.4.37

$P_{N_2O_3} = 1.90\text{ atm}$ and $P_{NO} = P_{NO_2} = 1.90\text{ atm}$

4.E.4.72: Q13.4.38

A 1.00-L vessel at 400 °C contains the following equilibrium concentrations: N_2, 1.00 M; H_2, 0.50 M; and NH_3, 0.25 M. How many moles of hydrogen must be removed from the vessel to increase the concentration of nitrogen to 1.1 M?

4.E.4.73: Q13.4.39

A 0.010 M solution of the weak acid HA has an osmotic pressure (see chapter on solutions and colloids) of 0.293 atm at 25 °C. A 0.010 M solution of the weak acid HB has an osmotic pressure of 0.345 atm under the same conditions.

(a) Which acid has the larger equilibrium constant for ionization

$$\text{HA } [\mathrm{HA}(aq) \rightleftharpoons \mathrm{A}^-(aq) + \mathrm{H}^+(aq)] \text{ or HB } [\mathrm{HB}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{B}^-(aq)] \text{ ?}$$

(b) What are the equilibrium constants for the ionization of these acids?

(Hint: Remember that each solution contains three dissolved species: the weak acid (HA or HB), the conjugate base (A^- or B^-), and the hydrogen ion (H^+). Remember that osmotic pressure (like all colligative properties) is related to the total number of solute particles. Specifically for osmotic pressure, those concentrations are described by molarities.)

4.E.4.74: S13.4.39

(a) HB ionizes to a greater degree and has the larger K_c.

(b) $K_c(\mathrm{HA}) = 5 \times 10^{-4}$

$K_c(\mathrm{HB}) = 3 \times 10^{-3}$

CHAPTER OVERVIEW

5: Acid-Base Equilibria

5.1: Brønsted-Lowry Acids and Bases

Learning Objectives

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

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 Svante 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.

In an earlier chapter on chemical reactions, we defined acids and bases as Arrhenius did: We identified an acid as a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions (OH^-). This definition is not wrong; it is simply limited.

5.1.1: Brønsted-Lowry Acids and Bases

Around 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry proposed a more general definition for acids and bases. 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. Bases 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:

$$H^+ + OH^- \rightarrow H_2O \tag{5.1.1}$$

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):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base} \tag{5.1.2}$$

$$HF \rightleftharpoons H^+ + F^- \tag{5.1.3}$$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \tag{5.1.4}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{5.1.5}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \tag{5.1.6}$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \tag{5.1.7}$$

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):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid} \tag{5.1.8}$$

$$OH^- + H^+ \rightleftharpoons H_2O \tag{5.1.9}$$

$$H_2O + H^+ \rightleftharpoons H_3O^+ \tag{5.1.10}$$

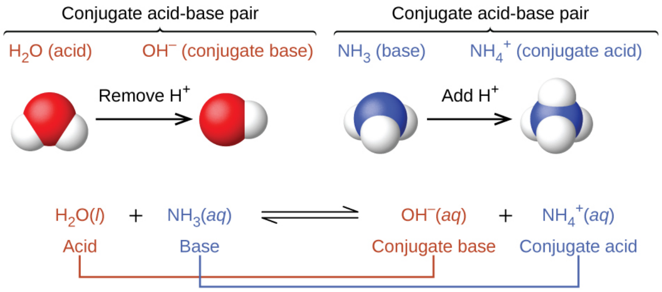
$$NH_3 + H^+ \rightleftharpoons NH_4^+ \tag{5.1.11}$$

$$S^{2-} + H^+ \rightleftharpoons HS^- \tag{5.1.12}$$

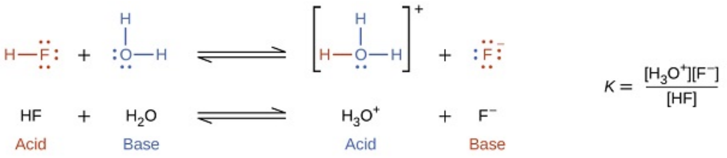
$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \tag{5.1.13}$$

$$F^- + H^+ \rightleftharpoons HF \tag{5.1.14}$$

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:



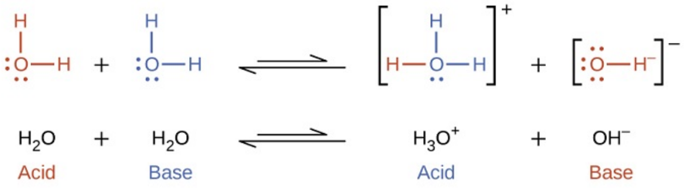
When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:

$$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^- \tag{5.1.15}$$

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.

5.1.2: Autoionization of Water

In the two previous examples (HF and C_5H_5N), we see 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):

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \quad K_w = [H_3O^+][OH^-] \tag{5.1.16}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, Kw 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 50-times larger than the value at 25 °C.

✓ Example 5.1.1: 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:

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^2 = [OH^-]^2 = 1.0 \times 10^{-14} \tag{5.1.17}$$

So:

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M \tag{5.1.18}$$

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 5.1.1

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 5.1.2 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

✓ Example 5.1.2: 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:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \tag{5.1.19}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{5.1.20}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

$$[\mathrm{OH^-}] = \frac{K_\mathrm{w}}{[\mathrm{H_3O^+}]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9} \tag{5.1.21}$$

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 $[\mathrm{OH^-}]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$\begin{aligned} K_\mathrm{w} &= [\mathrm{H_3O^+}][\mathrm{OH^-}] \\ &= (2.0 \times 10^{-6})(5.0 \times 10^{-9}) \\ &= 1.0 \times 10^{-14} \end{aligned}$$

? Exercise 5.1.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[\mathrm{H_3O^+}] = 1 \times 10^{-11} M \tag{5.1.22}$$

5.1.3: Amphiprotic 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:

$$\mathrm{HCO^-_{3(\mathit{aq})}} + \mathrm{H_2O_{(\mathit{l})}} \rightleftharpoons \mathrm{CO^{2-}_{3(\mathit{aq})}} + \mathrm{H_3O^+_{(\mathit{aq})}} \tag{5.1.23}$$

$$\mathrm{HCO^-_{3(\mathit{aq})}} + \mathrm{H_2O_{(\mathit{l})}} \rightleftharpoons \mathrm{H_2CO_{3(\mathit{aq})}} + \mathrm{OH^-_{(\mathit{aq})}} \tag{5.1.24}$$

✓ Example 5.1.3: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of $\mathrm{HSO_3^-}$

a. as an acid with $\mathrm{OH^-}$
b. as a base with HI

Solution

a. $\mathrm{HSO_3^-}(aq) + \mathrm{OH^-}(aq) \rightleftharpoons \mathrm{SO_3^{2-}}(aq) + \mathrm{H_2O_{(\mathit{l})}}$
b. $\mathrm{HSO_3^-}(aq) + \mathrm{HI}(aq) \rightleftharpoons \mathrm{H_2SO_3}(aq) + \mathrm{I^-}(aq)$

? Exercise 5.1.3

Write separate equations representing the reaction of $\mathrm{H_2PO_4^-}$

a. as a base with HBr
b. as an acid with $\mathrm{OH^-}$

Answer a

$$\mathrm{H_2PO_4^-}(aq) + \mathrm{HBr}(aq) \rightleftharpoons \mathrm{H_3PO_4}(aq) + \mathrm{Br^-}(aq)$$

Answer b

$$\mathrm{H_2PO_4^-}(aq) + \mathrm{OH^-}(aq) \rightleftharpoons \mathrm{HPO_4^{2-}}(aq) + \mathrm{H_2O_{(\mathit{l})}}$$

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:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{5.1.25}$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ C \tag{5.1.26}$$

5.1.4: Key Equations

- $$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \; (\text{at } 25\ ^\circ C) \tag{5.1.27}$$

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

5.2: pH and pOH

Learning Objectives

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

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:

$$\mathrm{pX} = -\log \mathrm{X} \tag{5.2.1}$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \tag{5.2.2}$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} \tag{5.2.3}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] \tag{5.2.4}$$

or

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}} \tag{5.2.5}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{5.2.6}$$

$$-\log K_\mathrm{w} = -\log([\mathrm{H_3O^+}][\mathrm{OH^-}]) = -\log[\mathrm{H_3O^+}] + -\log[\mathrm{OH^-}] \tag{5.2.7}$$

$$\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH} \tag{5.2.8}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = \mathrm{pH} + \mathrm{pOH} \tag{5.2.9}$$

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:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{5.2.10}$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{5.2.11}$$

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).

When $pH = 7$ Solutions are not Neutral

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:

$$\begin{aligned} pH &= -\log[\mathrm{H_3O^+}] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

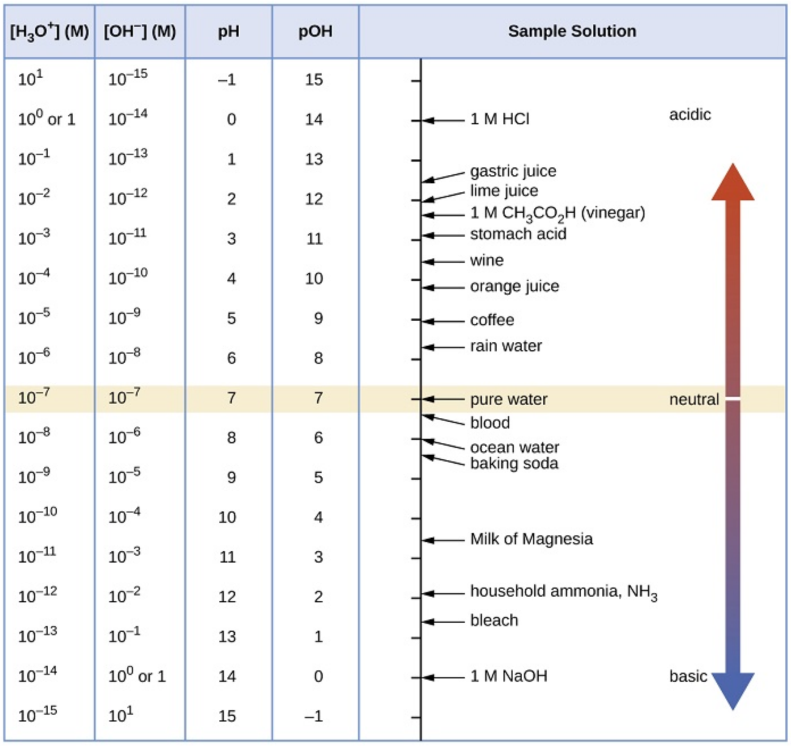
$$\begin{aligned} pOH &= -\log[\mathrm{OH^-}] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

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 5.2.1).

Table 5.2.1: Summary of Relations for Acidic, Basic and Neutral Solutions

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7
neutral	$[H_3O^+] = [OH^-]$	pH = 7
basic	$[H_3O^+] < [OH^-]$	pH > 7

Figure 5.2.1 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 5.2.1: 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 5.2.1: 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

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) \\ &= 2.92 \end{aligned}$$

? Exercise 5.2.1

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$\mathrm{CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)}$$

Air-saturated water has a hydronium ion concentration caused by the dissolved $\mathrm{CO_2}$ 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 5.2.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3 (slightly alkaline).

Solution

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = 7.3$$

$$\log[\mathrm{H_3O^+}] = -7.3$$

$$[\mathrm{H_3O^+}] = 10^{-7.3}$$

or

$$[\mathrm{H_3O^+}] = \text{antilog of} - 7.3$$

$$[\mathrm{H_3O^+}] = 5 \times 10^{-8}\ M$$

(On a calculator take the antilog, or the “inverse” log, of −7.3, or calculate $10^{-7.3}$.)

Exercise 5.2.2

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Answer

12 M

Example 5.2.3: Calculation of pOH

What are the pOH and the pH of a 0.0125-M solution of potassium hydroxide, KOH?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[\mathrm{OH^-}]$ = 0.0125 M:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log 0.0125 \tag{5.2.12}$$

$$= -(-1.903) = 1.903 \tag{5.2.13}$$

The pH can be found from the pOH:

$$\mathrm{pH} + \mathrm{pOH} = 14.00 \tag{5.2.14}$$

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 1.903 = 12.10 \tag{5.2.15}$$

Exercise 5.2.3

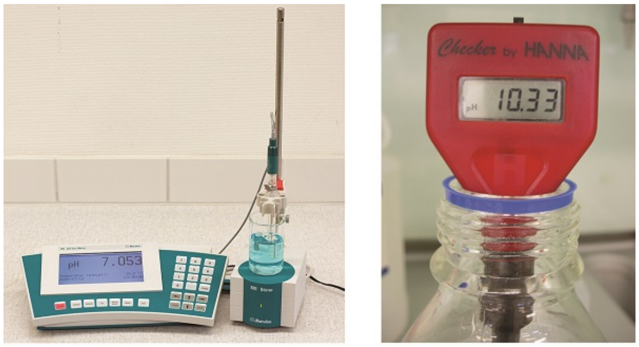
The hydronium ion concentration of vinegar is approximately $4 \times 10^{-3}\ M$. What are the corresponding values of pOH and pH?

Answer

pOH = 11.6,

pH = 14.00 - pOH = 2.4

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 5.2.2).



(a) (b)

Figure 5.2.2: (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)

The pH of a solution may also be visually estimated using colored indicators (Figure 5.2.3).

(a) (b)

Figure 5.2.3: (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

5.2.1: Key Equations

- $\mathrm{pH} = -\log[\mathrm{H_3O^+}]$
- $\mathrm{pOH} = -\log[\mathrm{OH^-}]$
- $[H_3O^+] = 10^{-\mathrm{pH}}$
- $[OH^-] = 10^{-\mathrm{pOH}}$
- $\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_w = 14.00$ 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

---

5.3: Relative Strengths of Acids

Learning Objectives

- Distinguish between strong and weak acids
- Assess the relative strengths of acids according to their ionization constants

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:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{5.3.1}$$

In these reactions, 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.

5.3.1: Strong Acid Ionization

A strong acid yields 100% (or very nearly so) of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ when the acid ionizes in water; Table $5.3.1$ lists several strong acids. A weak acid gives small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Table $5.3.1$: 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

Because strong acids ionize completely in water, the pH of a strong acid solution can be found using the acid concentration.

$$[\mathrm{HA}] = [\mathrm{H_3O^+}] \tag{5.3.2}$$

Example $5.3.1$

What is the pH of concentrated hydrochloric acid, a 12.1 M solution?

Solution

Because hydrochloric acid is a strong acid, we know that $[\mathrm{HCl}]$ is equal to the hydronium concentration $[\mathrm{H_3O^+}]$.

$$[\mathrm{HCl}] = [\mathrm{H_3O^+}] = 12.1\ M \tag{5.3.3}$$

$$pH = -log(12.1) = -1.083 \tag{5.3.4}$$

The pH of concentrated HCl is -1.083.

Exercise $5.3.1$

What is the pH of a 0.075 M solution of nitric acid?

Answer

pH = 1.12

5.3.2: The Ionization of Weak Acids

Many acids 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 non-ionized acid, hydronium ion, and the conjugate base of the acid, with the non-ionized acid present in the greatest concentration. 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:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{5.3.5}$$

we write the equation for the ionization constant as:

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \tag{5.3.6}$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so its activity has a value of 1, which does not change the value of K_a.

Acetic acid ($\mathrm{CH_3CO_2H}$) is a familiar example of 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 non-ionized (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 $5.3.1$). The remaining weak acid is present in the non-ionized 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 $5.3.1$: pH paper indicates that a 0.l-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 $\mathrm{CH_3CO_2H}$ (beaker on right) has a pH of 3 ($[\mathrm{H_3O^+}]$ = 0.001 M) because the weak acid $\mathrm{CH_3CO_2H}$ is only partially ionized. In this solution, $[\mathrm{H_3O^+}] < [\mathrm{CH_3CO_2H}]$. (credit: modification of work by Sahar Atwa)

Table $5.3.2$ gives the ionization constants for several weak acids; additional ionization constants can be found in the appendix of this text. Notice that all of the K_a values for weak acids are smaller than 1, indicating that the reactants side of the equilibrium reaction is favored. This is consistent with our definition of a weak acid: an acid that only partially ionizes in solution.

The strength of weak acids can be compared through their K_a values. 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 non-ionized acid, HA. Thus a stronger acid has a larger ionization constant than does a weaker acid.

Table $5.3.2$: Ionization Constants of Some Weak Acids

Ionization Reaction	K_a at 25 °C
$\mathrm{HSO_4^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{SO_4^{2-}}$	1.2×10^{-2}

Ionization Reaction	K_a at 25 °C
$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	3.5 × 10^{-4}
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	4.6 × 10^{-4}
$HNCO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	2 × 10^{-4}
$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$	1.8 × 10^{-4}
$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$	1.8 × 10^{-5}
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	2.9 × 10^{-8}
$HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-$	2.8 × 10^{-9}
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9 × 10^{-10}

✓ Example 5.3.2: 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 5.3.2

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 $HSO_4^- = 1.2 \times \times 10^{-2}$

Summary

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid ionization constants. 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. S

5.3.3: Key Equations

- $K_a = \frac{[H_3O^+][A^-]}{[HA]}$

Glossary

acid ionization constant (K_a)

equilibrium constant for the ionization of a weak acid

5.4: pH Calculations for Weak Acids

Learning Objectives

- Carry out equilibrium calculations for weak acid systems
- Determine the pH of a weak acid solution based on acid concentration and the acid ionization constant
- Calculate percent ionization for an acid

5.4.1: Acid Equilibrium Calculations

Acid equilibrium problems are one type of aqueous equilibrium reaction, and we can use the acid ionization constants (Ka) to quantitatively determine the concentrations of the acid, hydronium ions, and the conjugate base. Example $5.4.1$ demonstrates how an ICE table can be used for find equilibrium concentrations. To determine the pH of the solution at equilibrium we can use the equilibrium proton concentration, $[\mathrm{H_3O^+}]$, from the ICE table.

Example $5.4.1$: 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?

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq) \qquad K_\mathrm{a} = 1.8 \times 10^{-4}$$

Solution

1. Determine x and equilibrium concentrations. The equilibrium expression is:

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq)$$

Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction so we do not need to consider it 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 ⇌	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:

$$K_\mathrm{a} = 1.8 \times 10^{-4} = \frac{[\mathrm{H_3O^+}][\mathrm{HCO_2^-}]}{[\mathrm{HCO_2H}]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

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:

$$K_\mathrm{a} = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

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:

$$\begin{aligned} [\mathrm{H_3O^+}] &= 0 + x = 0 + 9.8 \times 10^{-3}\ M. \\ &= 9.8 \times 10^{-3}\ M \end{aligned}$$

The pH of the solution can be found by taking the negative log of the $[\mathrm{H_3O^+}]$, so:

$$pH = -\log(9.8 \times 10^{-3}) = 2.01$$

? Exercise 5.4.1: 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?

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \quad K_\mathrm{a} = 1.8 \times 10^{-5}$$

Hint

Determine $[\mathrm{CH_3CO_2^-}]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or $\frac{[\mathrm{CH_3CO_2^-}]}{[\mathrm{CH_3CO_2H}]_\mathrm{initial}} \times 100$.

Answer

percent ionization = 1.3%

Some weak acids 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.

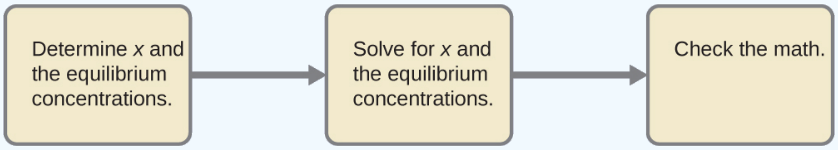
✓ Example 5.4.2: Equilibrium Concentrations in a Solution of a Weak Acid

Sodium bisulfate, $NaHSO_4$, is used in some household cleansers because it contains the $\mathrm{HSO_4^-}$ ion, a weak acid. What is the pH of a 0.50-*M* solution of $\mathrm{HSO_4^-}$?

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq) \quad K_\mathrm{a} = 1.2 \times 10^{-2}$$

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 $\rightleftharpoons$	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:

$$\frac{x}{[HSO_4^-]_i} \overset{?}{\le} 0.05$$

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:

$$\begin{aligned} [\mathrm{H_3O^+}] &= 0 + x = 0 + 7.2 \times 10^{-2}\ M \\ &= 7.2 \times 10^{-2}\ M \end{aligned}$$

The pH of this solution is:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log 7.2 \times 10^{-2} = 1.14$$

5.4.2: Percent Ionization of Acids

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:

$$\%\ \text{ionization} = \frac{[\mathrm{H_3O^+}]_{\mathrm{eq}}}{[\mathrm{HA}]_0} \times 100\% \tag{5.4.1}$$

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 5.4.3: 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:

$$\frac{[\mathrm{H_3O^+}]_{\mathrm{eq}}}{[\mathrm{HNO_2}]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NO_2^-}(aq) + \mathrm{H_3O^+}(aq).$$

Since $10^{-pH} = [\mathrm{H_3O^+}]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}\ M$, so that percent ionization (Equation 5.4.1) 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 5.4.3

Calculate the percent ionization of a 0.10 *M* solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

5.4.3: Summary

The strengths of Brønsted-Lowry acids in aqueous solutions can be determined by their acid ionization constants. Weak acids are only partially ionized in water. The pH of an acid solution can be determined using the concentration of the acid and the its acid ionization constant.

5.4.4: Key Equations

- $K_a = \frac{[H_3O^+][A^-]}{[HA]}$
- $\text{Percent ionization} = \frac{[H_3O^+]_{eq}}{[HA]_0} \times 100$

Glossary

acid ionization constant (K_a)

equilibrium constant for the ionization of a weak acid

percent ionization

ratio of the concentration of the ionized acid to the initial acid concentration, times 100

5.5: Relative Strengths of Bases

Learning Objectives

- Assess the relative strengths of bases according to their ionization constants
- Carry out equilibrium calculations for weak acid–base systems
- Calculate the K_b for the conjugate base of a weak acid

Bases act as proton acceptors. When in aqueous solutions, the water solvent can act as the acid that donates the proton to a base. 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:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq), \tag{5.5.1}$$

we write the equation for the ionization constant as:

$$K_\mathrm{b} = \frac{[\mathrm{HB^+}][\mathrm{OH^-}]}{[\mathrm{B}]} \tag{5.5.2}$$

where the concentrations are those at equilibrium. Again, we do not see water in the equation because water is the solvent and has an activity of 1.

A strong base yields 100% (or very nearly so) of OH^- and HB^+ when it reacts with water, while a weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH and $Ca(OH)_2$ are considered strong bases because they dissociate completely when dissolved in water.

✓ Example 5.5.1: 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*, $[\mathrm{C_8H_{10}N_4O_2H^+}] = 5.0 \times 10^{-3}$ *M*, and $[OH^-] = 2.5 \times 10^{-3}$ *M*?

Solution

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$\mathrm{C_8H_{10}N_4O_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{C_8H_{10}N_4O_2H^+}(aq) + \mathrm{OH^-}(aq)$$

so

$$K_\mathrm{b} = \frac{[\mathrm{C_8H_{10}N_4O_2H^+}][\mathrm{OH^-}]}{[\mathrm{C_8H_{10}N_4O_2}]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4} \tag{5.5.3}$$

? Exercise 5.5.1

What is the equilibrium constant for the ionization of the $\mathrm{HPO_4^{2-}}$ ion, a weak base:

$$\mathrm{HPO_4^{2-}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2PO_4^-}(aq) + \mathrm{OH^-}(aq)$$

In a solution containing a mixture of $\mathrm{NaH_2PO_4}$ and $\mathrm{Na_2HPO_4}$ at equilibrium with:

- $[\mathrm{OH^-}] = 1.3 \times 10^{-6}\, M$
- $[\mathrm{H_2PO_4^-}]{=}0 \cdot 042\ \mathrm{M}$ and
- $[\mathrm{HPO_4^{2\,-}}]{=}0 \cdot 341\ \mathrm{M}.$

Answer

K_b for $\mathrm{HPO_4^{2-}} = 1.6 \times 10^{-7}$

Exercise 5.5.2

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

$$K_b = 1.8 \times 10^{-5}$$

5.5.1: pH Calculations for Strong and Weak Bases

To determine the pH of a solution containing a strong base, the concentration of hydroxide ions, $[\mathrm{OH}-]$, is used to find the pOH.

$$pOH = -log[\mathrm{OH}-]$$

The pH and pOH are related through Kw, and so pH can be determined.

$$pH + pOH = 14$$

Weak bases cause only partial ionization. To determine the pH of a weak base solution we must utilize the base ionization constant. The reaction of a base, B, is:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB}^+(aq) + \mathrm{OH}^-(aq), \tag{5.5.4}$$

For example, a solution of the weak base trimethylamine, $(CH_3)_3N$, in water reacts according to the equation:

$$(\mathrm{CH_3})_3\mathrm{N}(aq) + \mathrm{H_2O}(l) \rightleftharpoons (\mathrm{CH_3})_3\mathrm{NH}^+(aq) + \mathrm{OH}^-(aq)$$

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 5.5.1). 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:

$$K_\mathrm{b} = \frac{[(\mathrm{CH_3})_3\mathrm{NH}^+][\mathrm{OH}^-]}{[(\mathrm{CH_3})_3\mathrm{N}]}$$

Figure 5.5.1: 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).

Table 5.5.1 contains ionization reactions and base ionization constants for select weak bases.

Table 5.5.1: Ionization Constants of Some Weak Bases

Ionization Reaction	K_b at 25 °C
$(\mathrm{CH_3})_2\mathrm{NH} + \mathrm{H_2O} \rightleftharpoons (\mathrm{CH_3})_2\mathrm{NH_2^+} + \mathrm{OH^-}$	5.9×10^{-4}
$\mathrm{CH_3NH_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{CH_3NH_3^+} + \mathrm{OH^-}$	4.4×10^{-4}

Ionization Reaction	K_b at 25 °C
$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$	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}

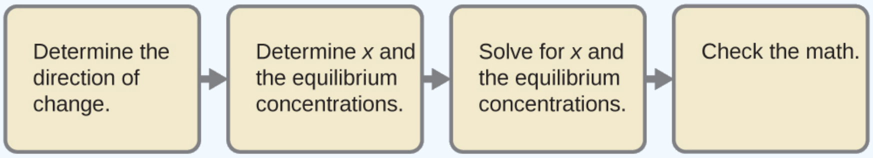
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

✓ Example 5.5.2: 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 5.5.6. 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	$\rightleftharpoons (CH_3)_3NH^+$	+ 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:

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 2.37 = 11.60$$

Check the work. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

5.5.2: Percent Ionization for Bases

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.

$$\%\text{ ionization} = \frac{[\mathrm{BH}^+]_{\mathrm{eq}}}{[\mathrm{B}]_0} \times 100\% \tag{5.5.5}$$

Exercise 5.5.3

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 $\frac{[\mathrm{NH}_4^+]}{[\mathrm{NH}_3]} \times 100\%$

Answer

$7.56 \times 10^{-4}\ M$, 2.33%

5.5.3: Ionization Constants for Conjugate Acid Base Pairs

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 $\mathrm{H_3O^+}$ 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 $\mathrm{H_3O^+}$—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases.

In an aqueous solution, the acid ionization constant for a particular acid (K_a) and the base ionization constant (K_b) for its conjugate base are related though K_w. Consider the ionization reactions for a conjugate acid-base pair, $\mathrm{HA} - \mathrm{A}^-$:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A}^-(aq) \tag{5.5.6}$$

with $K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A}^-]}{[\mathrm{HA}]}$.

$$\mathrm{A}^-(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OH}^-(aq) + \mathrm{HA}(aq) \tag{5.5.7}$$

with $K_\mathrm{b} = \frac{[\mathrm{HA}][\mathrm{OH}]}{[\mathrm{A}^-]}$.

Adding these two chemical equations yields the equation for the autoionization for water:

$$\begin{aligned} \mathrm{HA}\cancel{(aq)} + \mathrm{H_2O}(l) + \mathrm{A}^-\cancel{(aq)} + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A}^-\cancel{(aq)} + \mathrm{OH}^-(aq) + \mathrm{HA}\cancel{(aq)} \\ 2\,\mathrm{H_2O}(l) &\rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{OH}^-(aq) \end{aligned}$$

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:

$$K_\mathrm{a} \times K_\mathrm{b} = \frac{[\mathrm{H_3O^+}][\mathrm{A}^-]}{[\mathrm{HA}]} \times \frac{[\mathrm{HA}][\mathrm{OH}^-]}{[\mathrm{A}^-]} = [\mathrm{H_3O^+}][\mathrm{OH}^-] = K_\mathrm{w} \tag{5.5.8}$$

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 ($\mathrm{CH_3COO^-}$), is 5.6 × 10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_a \times K_b = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_w \tag{5.5.9}$$

✓ Example 5.5.3: 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:

$$\begin{aligned} K_a &= \frac{K_w}{K_b} \\ &= \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}} \\ &= 4.6 \times 10^{-4} \end{aligned}$$

This answer can be verified by finding the K_a for HNO_2 in Table E1

? Exercise 5.5.4

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}).

5.5.4: 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 [$H_2SeO_4 < H_2SO_4$].

5.5.5: Key Equations

- $K_b = \frac{[HB^+][OH^-]}{[B]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w \text{ (at room temperature)}$
- $\text{Percent ionization} = \frac{[BH^+]_{eq}}{[B]_0} \times 100$

Glossary

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/base to the initial acid/base concentration, times 100

5.6: Relating Structure to Acidity and Basicity

Learning Objectives

- Rationalize trends in acid–base strength in relation to molecular structure

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 $\mathrm{HCl} < \mathrm{HBr} < \mathrm{HI}$, 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:

$$\mathrm{O}^{2-}(aq) + \mathrm{H}_2\mathrm{O}(l) \longrightarrow \mathrm{OH}^-(aq) + \mathrm{OH}^-(aq) \tag{5.6.1}$$

$$\mathrm{NH}_2^-(aq) + \mathrm{H}_2\mathrm{O}(l) \longrightarrow \mathrm{NH}_3(aq) + \mathrm{OH}^-(aq) \tag{5.6.2}$$

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 $\mathrm{HF} < \mathrm{HCl} < \mathrm{HBr} < \mathrm{HI}$. 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 $\mathrm{CH}_4 < \mathrm{NH}_3 < \mathrm{H}_2\mathrm{O} < \mathrm{HF}$; across the third row, it is $\mathrm{SiH}_4 < \mathrm{PH}_3 < \mathrm{H}_2\mathrm{S} < \mathrm{HCl}$ (see Figure 5.6.1).

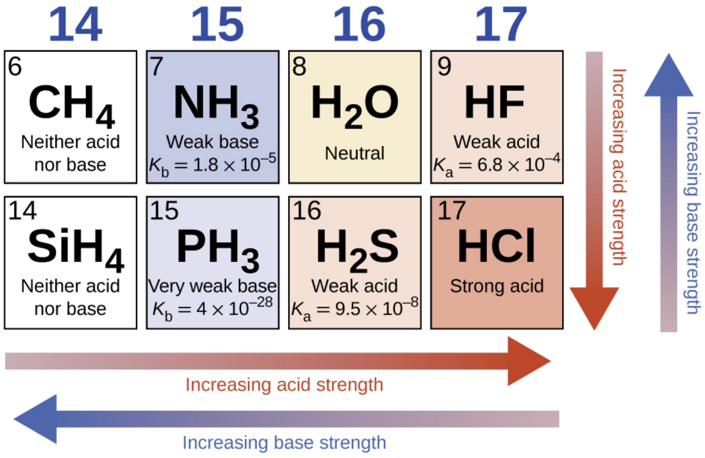
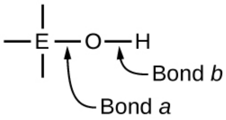


Figure 5.6.1: As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

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, $\mathrm{O}_2\mathrm{S(OH)}_2$, sulfurous acid, $\mathrm{OS(OH)}_2$, nitric acid, $\mathrm{O}_2\mathrm{NOH}$, perchloric acid, $\mathrm{O}_3\mathrm{ClOH}$, aluminum hydroxide, $\mathrm{Al(OH)}_3$, calcium hydroxide, $\mathrm{Ca(OH)}_2$, 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 5.6.2).

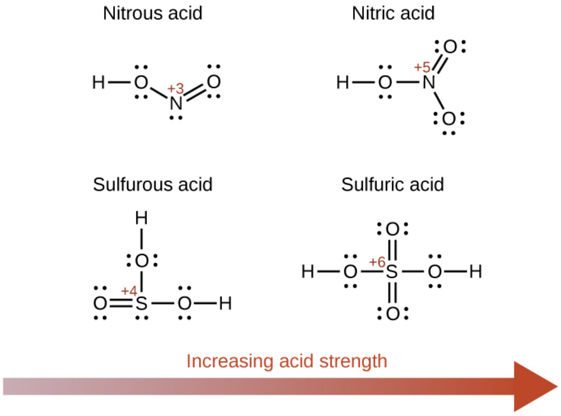


Figure 5.6.2: As the oxidation number of the central atom E increases, the acidity also increases.

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 $Al(H_2O)_3(OH)_3$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $Al(H_2O)_3(OH)_3$, is converted into the soluble ion, $[Al(H_2O)_2(OH)_4]^-$, by reaction with hydroxide ion:

$$[Al(H_2O)_3(OH)_3](aq) + OH^-(aq) \rightleftharpoons H_2O(l) + [Al(H_2O)_2(OH)_4]^-(aq)$$

In this reaction, a proton is transferred from one of the aluminum-bound H_2O molecules to a hydroxide ion in solution. The $Al(H_2O)_3(OH)_3$ 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 $[Al(H_2O)_6]^{3+}$ by reaction with hydronium ion:

$$3\,H_3O^+(aq) + Al(H_2O)_3(OH)_3(aq) \rightleftharpoons Al(H_2O)_6^{3+}(aq) + 3\,H_2O(l)$$

In this case, protons are transferred from hydronium ions in solution to $Al(H_2O)_3(OH)_3$, and the compound functions as a base.

Summary

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 [$H_2SeO_4 < H_2SO_4$].

5.6.1: Glossary

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

oxyacid

compound containing a nonmetal and one or more hydroxyl groups

5.7: Hydrolysis of Salt Solutions

Learning Objectives

- Predict whether a salt solution will be acidic, basic, or neutral
- Calculate the concentrations of the various species in a salt solution
- Describe the process that causes solutions of certain metal ions to be acidic

As we have seen in the section on chemical reactions, when an acid and base are mixed, they undergo a neutralization reaction. The word “neutralization” seems to imply that a stoichiometrically equivalent solution of an acid and a base would be neutral. This is sometimes true, but the salts that are formed in these reactions may have acidic or basic properties of their own, as we shall now see.

5.7.1: Acid-Base Neutralization

A solution is neutral when it contains equal concentrations of hydronium and hydroxide ions. When we mix solutions of an acid and a base, an acid-base neutralization reaction occurs. However, even if we mix stoichiometrically equivalent quantities, we may find that the resulting solution is not neutral. It could contain either an excess of hydronium ions or an excess of hydroxide ions because the nature of the salt formed determines whether the solution is acidic, neutral, or basic. The following four situations illustrate how solutions with various pH values can arise following a neutralization reaction using stoichiometrically equivalent quantities:

1. A strong acid and a strong base, such as HCl(*aq*) and NaOH(*aq*) will react to form a neutral solution since the conjugate partners produced are of negligible strength:
$$\mathrm{HCl}(aq)+\mathrm{NaOH}(aq) \rightleftharpoons \mathrm{NaCl}(aq)+\mathrm{H_2O}(l) \tag{5.7.1}$$
2. A strong acid and a weak base yield a weakly acidic solution, not because of the strong acid involved, but because of the conjugate acid of the weak base.
3. A weak acid and a strong base yield a weakly basic solution. A solution of a weak acid reacts with a solution of a strong base to form the conjugate base of the weak acid and the conjugate acid of the strong base. The conjugate acid of the strong base is a weaker acid than water and has no effect on the acidity of the resulting solution. However, the conjugate base of the weak acid is a weak base and ionizes slightly in water. This increases the amount of hydroxide ion in the solution produced in the reaction and renders it slightly basic.
4. A weak acid plus a weak base can yield either an acidic, basic, or neutral solution. This is the most complex of the four types of reactions. When the conjugate acid and the conjugate base are of unequal strengths, the solution can be either acidic or basic, depending on the relative strengths of the two conjugates. Occasionally the weak acid and the weak base will have the *same* strength, so their respective conjugate base and acid will have the same strength, and the solution will be neutral. To predict whether a particular combination will be acidic, basic or neutral, tabulated K values of the conjugates must be compared.

5.7.2: Salts of Weak Bases and Strong Acids

When we neutralize a weak base with a strong acid, the product is a salt containing the conjugate acid of the weak base. This conjugate acid is a weak acid. For example, ammonium chloride, NH_4Cl, is a salt formed by the reaction of the weak base ammonia with the strong acid HCl:

$$\mathrm{NH_3}(aq)+\mathrm{HCl}(aq) \longrightarrow \mathrm{NH_4Cl}(aq) \tag{5.7.2}$$

A solution of this salt contains ammonium ions and chloride ions. The chloride ion has no effect on the acidity of the solution since HCl is a strong acid. Chloride is a very weak base and will not accept a proton to a measurable extent. However, the ammonium ion, the conjugate acid of ammonia, reacts with water and increases the hydronium ion concentration:

$$\mathrm{NH_4^+}(aq)+\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq)+\mathrm{NH_3}(aq) \tag{5.7.3}$$

The equilibrium equation for this reaction is simply the ionization constant. K_a, for the acid NH_4^+:

$$\frac{[\mathrm{H_3O^+}][\mathrm{NH_3}]}{[\mathrm{NH_4^+}]}=K_\mathrm{a} \tag{5.7.4}$$

We will not find a value of K_a for the ammonium ion in Table E1. However, it is not difficult to determine K_a for NH_4^+ from the value of the ionization constant of water, K_w, and K_b, the ionization constant of its conjugate base, NH_3, using the following relationship:

$$K_w = K_a \times K_b \tag{5.7.5}$$

This relation holds for any base and its conjugate acid or for any acid and its conjugate base.

✓ Example 5.7.1: pH of a Solution of a Salt of a Weak Base and a Strong Acid

Aniline is an amine that is used to manufacture dyes. It is isolated as aniline hydrochloride, $[C_6H_5NH_3^+]Cl$, a salt prepared by the reaction of the weak base aniline and hydrochloric acid. What is the pH of a 0.233 *M* solution of aniline hydrochloride?

$$C_6H_5NH_3^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5NH_2(aq) \tag{5.7.6}$$

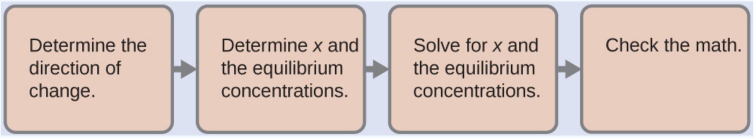
Solution

The new step in this example is to determine K_a for the $C_6H_5NH_3^+$ ion. The $C_6H_5NH_3^+$ ion is the conjugate acid of a weak base. The value of K_a for this acid is not listed in Table E1, but we can determine it from the value of K_b for aniline, $C_6H_5NH_2$, which is given as 4.6×10^{-10} :

$$K_a(\text{for } C_6H_5NH_3^+) \times K_b(\text{for } C_6H_5NH_2) = K_w = 1.0 \times 10^{-14} \tag{5.7.7}$$

$$K_a(\text{for } C_6H_5NH_3^+) = \frac{K_w}{K_b(\text{for } C_6H_5NH_2)} = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-10}} = 2.3 \times 10^{-5} \tag{5.7.8}$$

Now we have the ionization constant and the initial concentration of the weak acid, the information necessary to determine the equilibrium concentration of H_3O^+, and the pH:



With these steps we find $[H_3O^+] = 2.3 \times 10^{-3}$ *M* and pH = 2.64

? Exercise 5.7.1

What is the hydronium ion concentration in a 0.100-*M* solution of ammonium nitrate, NH_4NO_3, a salt composed of the ions NH_4^+ and NO_3^-. The K_b for the ammonia is 1.8×10^{-5}.

Answer

$K_a(\text{for } NH_4^+) = 5.6 \times 10^{-10}$, $[H_3O^+] = 7.5 \times 10^{-6}$ M

5.7.3: Salts of Weak Acids and Strong Bases

When we neutralize a weak acid with a strong base, we get a salt that contains the conjugate base of the weak acid. This conjugate base is usually a weak base. For example, sodium acetate, $NaCH_3CO_2$, is a salt formed by the reaction of the weak acid acetic acid with the strong base sodium hydroxide:

$$CH_3CO_2H(aq) + NaOH(aq) \longrightarrow NaCH_3CO_2(aq) + H_2O(aq) \tag{5.7.9}$$

A solution of this salt contains sodium ions and acetate ions. The sodium ion has no effect on the acidity of the solution. However, the acetate ion, the conjugate base of acetic acid, reacts with water and increases the concentration of hydroxide ion:

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq) \tag{5.7.10}$$

The equilibrium equation for this reaction is the ionization constant, K_b, for the base $CH_3CO_2^-$. The value of K_b can be calculated from the value of the ionization constant of water, K_w, and K_a, the ionization constant of the conjugate acid of the anion using the equation:

$$_{\mathrm{w}} = K_{\mathrm{a}} \times K_{\mathrm{b}} \tag{5.7.11}$$

For the acetate ion and its conjugate acid we have:

$$K_{\mathrm{b}}(\text{for } \mathrm{CH_3CO_2^-}) = \frac{K_{\mathrm{w}}}{K_{\mathrm{a}}(\text{for } \mathrm{CH_3CO_2H})} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \tag{5.7.12}$$

Some handbooks do not report values of K_{b}. They only report ionization constants for acids. If we want to determine a K_{b} value using one of these handbooks, we must look up the value of K_{a} for the conjugate acid and convert it to a K_{b} value.

✓ Example 5.7.2: Equilibrium of a Salt of a Weak Acid and a Strong Base

Determine the acetic acid concentration in a solution with $[\mathrm{CH_3CO_2^-}] = 0.050\ M$ and $[\mathrm{OH^-}] = 2.5 \times 10^{-6}\ M$ at equilibrium. The reaction is:

$$\mathrm{CH_3CO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2H}(aq) + \mathrm{OH^-}(aq) \tag{5.7.13}$$

Solution

We are given two of three equilibrium concentrations and asked to find the missing concentration. If we can find the equilibrium constant for the reaction, the process is straightforward.

The acetate ion behaves as a base in this reaction; hydroxide ions are a product. We determine K_{b} as follows:

$$K_{\mathrm{b}}(\text{for } \mathrm{CH_3CO_2^-}) = \frac{K_{\mathrm{w}}}{K_{\mathrm{a}}(\text{for } \mathrm{CH_3CO_2H})} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \tag{5.7.14}$$

Now find the missing concentration:

$$K_{\mathrm{b}} = \frac{[\mathrm{CH_3CO_2H}][\mathrm{OH^-}]}{[\mathrm{CH_3CO_2^-}]} = 5.6 \times 10^{-10} \tag{5.7.15}$$

$$= \frac{[\mathrm{CH_3CO_2H}](2.5 \times 10^{-6})}{(0.050)} = 5.6 \times 10^{-10} \tag{5.7.16}$$

Solving this equation we get $[\mathrm{CH_3CO_2H}] = 1.1 \times 10^{-5}\ M$.

? Exercise 5.7.2

What is the pH of a 0.083-*M* solution of $\mathrm{CN^-}$? Use 4.9×10^{-10} as K_{a} for HCN. Hint: We will probably need to convert pOH to pH or find $[\mathrm{H_3O^+}]$ using $[\mathrm{OH^-}]$ in the final stages of this problem.

Answer

11.16

5.7.4: Equilibrium in a Solution of a Salt of a Weak Acid and a Weak Base

In a solution of a salt formed by the reaction of a weak acid and a weak base, to predict the pH, we must know both the K_{a} of the weak acid and the K_{b} of the weak base. If $K_{\mathrm{a}} > K_{\mathrm{b}}$, the solution is acidic, and if $K_{\mathrm{b}} > K_{\mathrm{a}}$, the solution is basic.

✓ Example 5.7.3: Determining the Acidic or Basic Nature of Salts

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. KBr
b. $\mathrm{NaHCO_3}$
c. $\mathrm{NH_4Cl}$
d. $\mathrm{Na_2HPO_4}$
e. $\mathrm{NH_4F}$

Solution

Consider each of the ions separately in terms of its effect on the pH of the solution, as shown here:

a. The K^+ cation and the Br^- anion are both spectators, since they are the cation of a strong base (KOH) and the anion of a strong acid (HBr), respectively. The solution is neutral.
b. The Na^+ cation is a spectator, and will not affect the pH of the solution; the $\mathrm{HCO_3^-}$ anion is amphiprotic.The K_a of $\mathrm{HCO_3^-}$ is 4.7 × 10^{-11}, so the K_b of its conjugate base is $\frac{1.0\times10^{-14}}{4.7\times10^{-11}}=2.1\times10^{-4}$. Since $K_b >> K_a$, the solution is basic.
c. The $\mathrm{NH_4^+}$ ion is acidic and the Cl^- ion is a spectator. The solution will be acidic.
d. The Na^+ ion is a spectator and will not affect the pH of the solution, while the $\mathrm{HPO_4^{2-}}$ ion is amphiprotic. The K_a of $\mathrm{HPO_4^{2-}}$ is 4.2 × 10^{-13} and its K_b is $\frac{1.0\times10^{-14}}{4.2\times10^{-13}}=2.4\times10^{-2}$. Because $K_b >> K_a$, the solution is basic.
e. The $\mathrm{NH_4^+}$ ion is listed as being acidic, and the F^- ion is listed as a base, so we must directly compare the K_a and the K_b of the two ions. K_a of $\mathrm{NH_4^+}$ is 5.6 × 10^{-10}, which seems very small, yet the K_b of F^- is 1.4 × 10^{-11}, so the solution is acidic, since $K_a > K_b$.

Exercise 5.7.3

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. K_2CO_3
b. $CaCl_2$
c. KH_2PO_4
d. $(NH_4)_2CO_3$
e. $AlBr_3$

Answer a

basic

Answer b

neutral

Answer c

acidic

Answer d

basic

Answer e

acidic

5.7.5: The Ionization of Hydrated Metal Ions

If we measure the pH of the solutions of a variety of metal ions we will find that these ions act as weak acids when in solution. The aluminum ion is an example. When aluminum nitrate dissolves in water, the aluminum ion reacts with water to give a hydrated aluminum ion, $\mathrm{Al(H_2O)_6^{3+}}$, dissolved in bulk water. What this means is that the aluminum ion has the strongest interactions with the six closest water molecules (the so-called first solvation shell), even though it does interact with the other water molecules surrounding this $\mathrm{Al(H_2O)_6^{3+}}$ cluster as well:

$$\mathrm{Al(NO_3)_3}(s)+6\,\mathrm{H_2O}(l)\longrightarrow \mathrm{Al(H_2O)_6^{3+}}(aq)+3\,\mathrm{NO_3^-}(aq) \tag{5.7.17}$$

We frequently see the formula of this ion simply as "$Al^{3+}(aq)$", without explicitly noting the six water molecules that are the closest ones to the aluminum ion and just describing the ion as being solvated in water (hydrated). This is similar to the simplification of the formula of the hydronium ion, H_3O^+ to H^+. However, in this case, the hydrated aluminum ion is a weak acid (Figure 5.7.1) and donates a proton to a water molecule. Thus, the hydration becomes important and we may use formulas that show the extent of hydration:

$$\text{Al}(\text{H}_2\text{O})_6^{3+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}(aq) \quad K_\text{a} = 1.4 \times 10^{-5} \tag{5.7.18}$$

As with other polyprotic acids, the hydrated aluminum ion ionizes in stages, as shown by:

$$\text{Al}(\text{H}_2\text{O})_6^{3+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}(aq) \tag{5.7.19}$$

$$\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Al}(\text{H}_2\text{O})_4(\text{OH})_2^+(aq) \tag{5.7.20}$$

$$\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Al}(\text{H}_2\text{O})_3(\text{OH})_3(aq) \tag{5.7.21}$$

Note that some of these aluminum species are exhibiting amphiprotic behavior, since they are acting as acids when they appear on the left side of the equilibrium expressions and as bases when they appear on the right side.

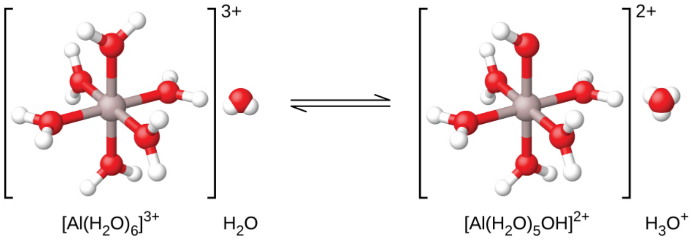


Figure 5.7.1: When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid.

The constants for the different stages of ionization are not known for many metal ions, so we cannot calculate the extent of their ionization. However, practically all hydrated metal ions other than those of the alkali metals ionize to give acidic solutions. Ionization increases as the charge of the metal ion increases or as the size of the metal ion decreases.

Summary

The characteristic properties of aqueous solutions of Brønsted-Lowry acids are due to the presence of hydronium ions; those of aqueous solutions of Brønsted-Lowry bases are due to the presence of hydroxide ions. The neutralization that occurs when aqueous solutions of acids and bases are combined results from the reaction of the hydronium and hydroxide ions to form water. Some salts formed in neutralization reactions may make the product solutions slightly acidic or slightly basic. Solutions that contain salts or hydrated metal ions have a pH that is determined by the extent of the hydrolysis of the ions in the solution. The pH of the solutions may be calculated using familiar equilibrium techniques, or it may be qualitatively determined to be acidic, basic, or neutral depending on the relative K_a and K_b of the ions involved.

5.E: Acid-Base Equilibria (Exercises)

5.E.1: Brønsted-Lowry Acids and Bases

1. Write equations that show NH_3 as both a conjugate acid and a conjugate base.

Answer

One example for NH_3 as a conjugate acid: $NH_2^- + H^+ \longrightarrow NH_3$; as a conjugate base: $NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)$

2. Write equations that show $H_2PO_4^-$ acting both as an acid and as a base.

3. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

a. H_3O^+
b. HCl
c. NH_3
d. CH_3CO_2H
e. NH_4^+
f. HSO_4^-

Answer

a. $H_3O^+(aq) \longrightarrow H^+(aq) + H_2O_{(l)}$;
b. $HCl(l) \longrightarrow H^+(aq) + Cl^-(aq)$;
c. $NH_3(aq) \longrightarrow H^+(aq) + NH_2^-(aq)$;
d. $CH_3CO_2H(aq) \longrightarrow H^+(aq) + CH_3CO_2^-(aq)$;
e. $NH_4^+(aq) \longrightarrow H^+(aq) + NH_3(aq)$;
f. $HSO_4^-(aq) \longrightarrow H^+(aq) + SO_4^{2-}(aq)$

4. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

a. HNO_3
b. PH_4^+
c. H_2S
d. CH_3CH_2COOH
e. $H_2PO_4^-$
f. HS^-

5. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

a. H_2O
b. OH^-
c. NH_3
d. CN^-
e. S^{2-}
f. $H_2PO_4^-$

Answer

a. $H_2O_{(l)} + H^+(aq) \longrightarrow H_3O^+(aq)$
b. $OH^-(aq) + H^+(aq) \longrightarrow H_2O_{(l)}$
c. $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$;
d. $CN^-(aq) + H^+(aq) \longrightarrow HCN(aq)$
e. $S^{2-}(aq) + H^+(aq) \longrightarrow HS^-(aq)$
f. $H_2PO_4^-(aq) + H^+(aq) \longrightarrow H_3PO_4(aq)$

6. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

   a. HS^-
   b. PO_4^{3-}
   c. NH_2^-
   d. C_2H_5OH
   e. O^{2-}
   f. $H_2PO_4^-$

7. What is the conjugate acid of each of the following? What is the conjugate base of each?

   a. OH^-
   b. H_2O
   c. HCO_3^-
   d. NH_3
   e. HSO_4^-
   f. H_2O_2
   g. HS^-
   h. $H_5N_2^+$

Answer

H_2O, O^{2-}; H_3O^+, OH^- ; H_2CO_3, CO_3^{2-}; NH_4^+, NH_2^-; H_2SO_4, SO_4^{2-}; $H_3O_2^+$, HO_2^-; H_2S; S^{2-}; $H_6N_2^{2+}$, H_4N_2

8. What is the conjugate acid of each of the following? What is the conjugate base of each?

   a. H_2S
   b. $H_2PO_4^-$
   c. PH_3
   d. HS^-
   e. HSO_3^-
   f. $H_3O_2^+$
   g. H_4N_2
   h. CH_3OH

9. Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

   a. $HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$
   b. $CN^- + H_2O \longrightarrow HCN + OH^-$
   c. $H_2SO_4 + Cl^- \longrightarrow HCl + HSO_4^-$
   d. $HSO_4^- + OH^- \longrightarrow SO_4^{2-} + H_2O$
   e. $O^{2-} + H_2O \longrightarrow 2\,OH^-$
   f. $[Cu(H_2O)_3(OH)]^+ + [Al(H_2O)_6]^{3+} \longrightarrow [Cu(H_2O)_4]^{2+} + [Al(H_2O)_5(OH)]^{2+}$
   g. $H_2S + NH_2^- \longrightarrow HS^- + NH_3$

Answer

The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA. HNO_3(BA), H_2O(BB), H_3O^+(CA), NO_3^-(CB); CN^-(BB), H_2O(BA), HCN(CA), OH^- (CB); H_2SO_4(BA), Cl^-(BB), HCl(CA), HSO_4^-(CB); HSO_4^-(BA), OH^-(BB), SO_4^{2-}(CB), H_2O(CA); O^{2-}(BB), H2O(BA) OH^- (CB and CA); $[Cu(H_2O)_3(OH)]^+$ (BB), $[Al(H_2O)_6]^{3+}$(BA), $[Cu(H_2O)_4]^{2+}$(CA), $[Al(H_2O)_5(OH)]^{2+}$(CB); H_2S(BA), NH_2^-(BB), HS^-(CB), NH_3(CA)

10. Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

   a. $NO_2^- + H_2O \longrightarrow HNO_2 + OH^-$
   b. $HBr + H_2O \longrightarrow H_3O^+ + Br^-$
   c. $HS^- + H_2O \longrightarrow H_2S + OH^-$

d. $H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O$
e. $H_2PO_4^- + HCl \longrightarrow H_3PO_4 + Cl^-$
f. $[Fe(H_2O)_5(OH)]^{2+} + [Al(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_6]^{3+} + [Al(H_2O)_5(OH)]^{2+}$
g. $CH_3OH + H^- \longrightarrow CH_3O^- + H_2$

11. What are amphiprotic species? Illustrate with suitable equations.

Answer

Amphiprotic species may either gain or lose a proton in a chemical reaction, thus acting as a base or an acid. An example is H_2O.

As an acid: $H_2O(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$.

As a base: $H_2O(aq) + HCl(aq) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

12. State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species:

a. H_2O
b. $H_2PO_4^-$
c. S^{2-}
d. CO_3^{2-}
e. HSO_4^-

13. State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.

a. NH_3
b. HPO_4^-
c. Br^-
d. NH_4^+
e. ASO_4^{3-}

Answer

amphiprotic: $NH_3 + H_3O^+ \longrightarrow NH_4OH + H_2O$, $NH_3 + OCH_3^- \longrightarrow NH_2^- + CH_3OH$; $HPO_4^{2-} + OH^- \longrightarrow PO_4^{3-} + H_2O$, $HPO_4^{2-} + HClO_4 \longrightarrow H_2PO_4^- + ClO_4^-$; not amphiprotic: Br^-; NH_4^+; AsO_4^{3-}

14. Is the self ionization of water endothermic or exothermic? The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C and 9.6×10^{-14} at 60 °C.

5.E.2: pH and pOH

15. Explain why a sample of pure water at 40 °C is neutral even though $[H_3O^+] = 1.7 \times 10^{-7}$ *M*. K_w is 2.9×10^{-14} at 40 °C.

Answer

In a neutral solution $[H_3O^+] = [OH^-]$. At 40 °C,

$[H_3O^+] = [OH^-] = (2.910^{-14})^{1/2} = 1.7 \times 10^{-7}$.

16. The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 40 °C.

17. The ionization constant for water (K_w) is 9.614×10^{-14} at 60 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 60 °C.

Answer

$x = 3.101 \times 10^{-7}$ M $= [H_3O^+] = [OH^-]$

pH = -log $3.101 \times 10^{-7} = -(-6.5085) = 6.5085$

pOH = pH = 6.5085

18. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

a. 0.200 M HCl
b. 0.0143 M NaOH
c. 3.0 M HNO_3
d. 0.0031 M $Ca(OH)_2$

19. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

a. 0.000259 M $HClO_4$
b. 0.21 M NaOH
c. 0.000071 M $Ba(OH)_2$
d. 2.5 M KOH

Answer

pH = 3.587; pOH = 10.413; pH = 0.68; pOH = 13.32; pOH = 3.85; pH = 10.15; pH = −0.40; pOH = 14.4

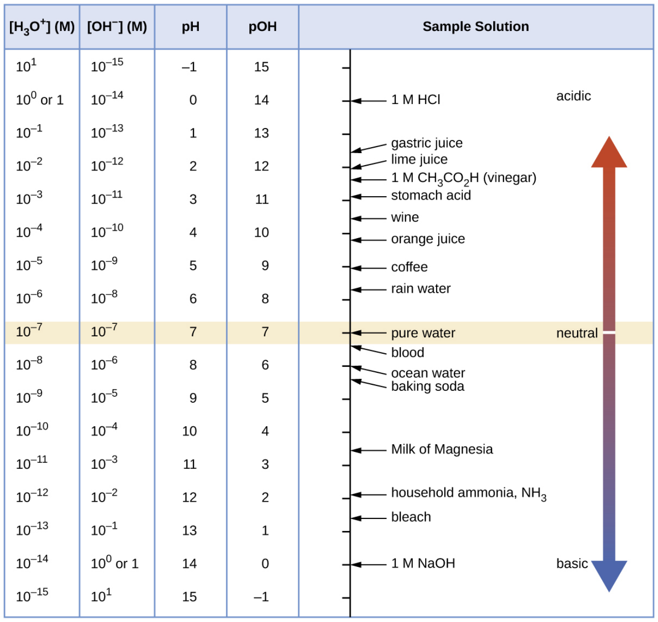
20. What are the pH and pOH of a solution of 2.0 M HCl, which ionizes completely?

21. What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

Answer

$[H_3O^+] = 3.0 \times 10^{-7}\ M$; $[OH^-] = 3.3 \times 10^{-8}\ M$

22. Calculate the hydrogen ion concentration and the hydroxide ion concentration in wine from its pH. See below Figure for useful information.



$[H_3O^+]$ (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

23. Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See Figure for useful information.

Answer

$[H_3O^+] = 1 \times 10^{-2}\ M$; $[OH^-] = 1 \times 10^{-12}\ M$

24. The hydronium ion concentration in a sample of rainwater is found to be $1.7 \times 10^{-6}\ M$ at 25 °C. What is the concentration of hydroxide ions in the rainwater?

25. The hydroxide ion concentration in household ammonia is $3.2 \times 10^{-3}\ M$ at 25 °C. What is the concentration of hydronium ions in the solution?

Answer

$[OH^-] = 3.1 \times 10^{-12}\ M$

5.E.3: Relative Strengths of Acids and Bases

5.E.3.1: Q14.3.1

Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.

5.E.3.2: Q14.3.2

Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.

The salt ionizes in solution, but the anion slightly reacts with water to form the weak acid. This reaction also forms OH^-, which causes the solution to be basic.

5.E.3.3: Q14.3.3

Use this list of important industrial compounds (and Figure) to answer the following questions regarding: CaO, $Ca(OH)_2$, CH_3CO_2H, CO_2, HCl, H_2CO_3, HF, HNO_2, HNO_3, H_3PO_4, H_2SO_4, NH_3, $NaOH$, Na_2CO_3.

a. Identify the strong Brønsted-Lowry acids and strong Brønsted-Lowry bases.
b. List those compounds in that can behave as Brønsted-Lowry acids with strengths lying between those of H_3O^+ and H_2O.
c. List those compounds in that can behave as Brønsted-Lowry bases with strengths lying between those of H_2O and OH^-.

5.E.3.4: Q14.3.4

The odor of vinegar is due to the presence of acetic acid, CH_3CO_2H, a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this acid.

5.E.3.5: S14.3.4

$[H_2O] > [CH_3CO_2H] > [H_3O^+] \approx [CH_3CO_2^-] > [OH^-]$

5.E.3.6: Q14.3.5

Household ammonia is a solution of the weak base NH_3 in water. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this base.

5.E.3.7: Q14.3.4

Explain why the ionization constant, K_a, for H_2SO_4 is larger than the ionization constant for H_2SO_3.

5.E.3.8: S14.3.4

The oxidation state of the sulfur in H_2SO_4 is greater than the oxidation state of the sulfur in H_2SO_3.

5.E.3.9: Q14.3.7

Explain why the ionization constant, K_a, for HI is larger than the ionization constant for HF.

5.E.3.10: Q14.3.8

Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $Mg(OH)_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction, and identify the conjugate acid-base pairs.

5.E.3.11: S14.3.8

$$\underset{\text{BB}}{Mg(OH)_2(s)} + \underset{\text{BA}}{HCl(aq)} \longrightarrow \underset{\text{CB}}{Mg^{2+}(aq)} + \underset{\text{CA}}{2\,Cl^-(aq)} + 2\,H_2O(l)$$

5.E.3.12: Q14.3.9

Nitric acid reacts with insoluble copper(II) oxide to form soluble copper(II) nitrate, $Cu(NO_3)_2$, a compound that has been used to prevent the growth of algae in swimming pools. Write the balanced chemical equation for the reaction of an aqueous solution of HNO_3 with CuO.

5.E.3.13: Q14.3.10

What is the ionization constant at 25 °C for the weak acid $CH_3NH_3^+$, the conjugate acid of the weak base CH_3NH_2, $K_b = 4.4 \times 10^{-4}$.

5.E.3.14: S14.3.10

$K_a = 2.3 \times 10^{-11}$

5.E.3.15: Q14.3.11

What is the ionization constant at 25 °C for the weak acid $(CH_3)_2NH_2^+$, the conjugate acid of the weak base $(CH_3)_2NH$, $K_b = 7.4 \times 10^{-4}$?

5.E.3.16: Q14.3.12

Which base, CH_3NH_2 or $(CH_3)_2NH$, is the strongest base? Which conjugate acid, $(CH_3)_2NH_2^+$ or $(CH_3)_2NH$, is the strongest acid?

5.E.3.17: S14.3.12

The strongest base or strongest acid is the one with the larger K_b or K_a, respectively. In these two examples, they are $(CH_3)_2NH$ and $CH_3NH_3^+$.

5.E.3.18: Q14.3.3

Which is the stronger acid, NH_4^+ or HBrO?

5.E.3.19: Q14.3.14

Which is the stronger base, $(CH_3)_3N$ or $H_2BO_3^-$?

5.E.3.20: S14.3.14

triethylamine.

5.E.3.21: Q14.3.15

Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.

a. H_2O or HF
b. $B(OH)_3$ or $Al(OH)_3$
c. HSO_3^- or HSO_4^-
d. NH_3 or H_2S
e. H_2O or H_2Te

5.E.3.22: Q14.3.16

Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.

a. HSO_4^- or $HSeO_4^-$
b. NH_3 or H_2O
c. PH_3 or HI
d. NH_3 or PH_3
e. H_2S or HBr

5.E.3.23: S14.3.16

a. HSO_4^-; higher electronegativity of the central ion. H_2O;
b. NH_3 is a base and water is neutral, or decide on the basis of K_a values. HI;
c. PH_3 is weaker than HCl; HCl is weaker than HI. Thus, PH_3 is weaker than HI.
d. PH_3; in binary compounds of hydrogen with nonmetals, the acidity increases for the element lower in a group.
e. HBr; in a period, the acidity increases from left to right; in a group, it increases from top to bottom. Br is to the left and below S, so HBr is the stronger acid.

5.E.3.24: Q14.3.17

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

a. acidity: HCl, HBr, HI
b. basicity: H_2O, OH^-, H^-, Cl^-
c. basicity: $Mg(OH)_2$, $Si(OH)_4$, $ClO_3(OH)$ (Hint: Formula could also be written as $HClO_4$).
d. acidity: HF, H_2O, NH_3, CH_4

5.E.3.25: Q14.3.18

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

a. acidity: $NaHSO_3$, $NaHSeO_3$, $NaHSO_4$
b. basicity: BrO_2^-, ClO_2^-, IO_2^-
c. acidity: HOCl, HOBr, HOI
d. acidity: HOCl, HOClO, $HOClO_2$, $HOClO_3$
e. basicity: NH_2^-, HS^-, HTe^-, PH_2^-
f. basicity: BrO^-, BrO_2^-, BrO_3^-, BrO_4^-

5.E.3.26: S14.3.18

a. $NaHSeO_3 < NaHSO_3 < NaHSO_4$; in polyoxy acids, the more electronegative central element—S, in this case—forms the stronger acid. The larger number of oxygen atoms on the central atom (giving it a higher oxidation state) also creates a greater release of hydrogen atoms, resulting in a stronger acid. As a salt, the acidity increases in the same manner.
b. $ClO_2^- < BrO_2^- < IO_2^-$; the basicity of the anions in a series of acids will be the opposite of the acidity in their oxyacids. The acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three.
c. HOI < HOBr < HOCl; in a series of the same form of oxyacids, the acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three.
d. HOCl < HOClO < $HOClO_2$ < $HOClO_3$; in a series of oxyacids of the same central element, the acidity increases as the number of oxygen atoms increases (or as the oxidation state of the central atom increases).
e. $HTe^- < HS^- << PH_2^- < NH_2^-$; PH_2^- and NH_2^- are anions of weak bases, so they act as strong bases toward H^+. HTe^- and HS^- are anions of weak acids, so they have less basic character. In a periodic group, the more electronegative element has the more basic anion.
f. $BrO_4^- < BrO_3^- < BrO_2^- < BrO^-$; with a larger number of oxygen atoms (that is, as the oxidation state of the central ion increases), the corresponding acid becomes more acidic and the anion consequently less basic.

5.E.3.27: Q14.3.19

Both HF and HCN ionize in water to a limited extent. Which of the conjugate bases, F^- or CN^-, is the stronger base? See Table.

5.E.3.28: Q14.3.20

The active ingredient formed by aspirin in the body is salicylic acid, $C_6H_4OH(CO_2H)$. The carboxyl group ($-CO_2H$) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001-*M* aqueous solution of $C_6H_4OH(CO_2H)$.

$$[\mathrm{H_2O}] > [\mathrm{C_6H_4OH(CO_2H)}] > [\mathrm{H^+}]_0 > [\mathrm{C_6H_4OH(CO_2)^-}] \gg [\mathrm{C_6H_4O(CO_2H)^-}] > [\mathrm{OH^-}]$$

What do we represent when we write:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)? \tag{5.E.1}$$

5.E.3.29: Q14.3.21

Explain why equilibrium calculations are not necessary to determine ionic concentrations in solutions of certain strong electrolytes such as NaOH and HCl. Under what conditions are equilibrium calculations necessary as part of the determination of the concentrations of all ions of some other strong electrolytes in solution?

5.E.3.30: S14.3.21

Strong electrolytes are 100% ionized, and, as long as the component ions are neither weak acids nor weak bases, the ionic species present result from the dissociation of the strong electrolyte. Equilibrium calculations are necessary when one (or more) of the ions is a weak acid or a weak base.

5.E.3.31: Q14.3.22

Are the concentrations of hydronium ion and hydroxide ion in a solution of an acid or a base in water directly proportional or inversely proportional? Explain your answer.

5.E.3.32: Q14.3.23

What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid?

5.E.3.33: S14.3.23

1. Assume that the change in initial concentration of the acid as the equilibrium is established can be neglected, so this concentration can be assumed constant and equal to the initial value of the total acid concentration.
2. Assume we can neglect the contribution of water to the equilibrium concentration of H_3O^+.

5.E.3.34: Q14.3.24

What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak base?

5.E.3.35: Q14.3.25

Which of the following will increase the percent of NH_3 that is converted to the ammonium ion in water (Hint: Use LeChâtelier's principle.)?

a. addition of NaOH
b. addition of HCl
c. addition of NH_4Cl

5.E.3.36: S14.3.25

The addition of HCl

5.E.3.37: Q14.3.26

Which of the following will increase the percent of HF that is converted to the fluoride ion in water?

a. addition of NaOH
b. addition of HCl
c. addition of NaF

5.E.3.38: Q14.3.27

What is the effect on the concentrations of NO_2^-, HNO_2, and OH^- when the following are added to a solution of KNO_2 in water:

a. HCl
b. HNO_2
c. NaOH
d. NaCl
e. KNO

The equation for the equilibrium is:

$$NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq) \tag{5.E.2}$$

5.E.3.39: S14.3.27

a. Adding HCl will add H_3O^+ ions, which will then react with the OH^- ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of HNO_2, and decreasing the concentration of NO_2^- ions.
b. Adding HNO_2 increases the concentration of HNO_2 and shifts the equilibrium to the left, increasing the concentration of NO_2^- ions and decreasing the concentration of OH^- ions.

c. Adding NaOH adds OH^- ions, which shifts the equilibrium to the left, increasing the concentration of NO_2^- ions and decreasing the concentrations of HNO_2.
d. Adding NaCl has no effect on the concentrations of the ions.
e. Adding KNO_2 adds NO_2^- ions and shifts the equilibrium to the right, increasing the HNO_2 and OH^- ion concentrations.

5.E.3.40: Q14.3.28

What is the effect on the concentration of hydrofluoric acid, hydronium ion, and fluoride ion when the following are added to separate solutions of hydrofluoric acid?

a. HCl
b. KF
c. NaCl
d. KOH
e. HF

The equation for the equilibrium is:

$$\mathrm{HF}(aq)+\mathrm{H_2O}(l)\rightleftharpoons \mathrm{H_3O^+}(aq)+\mathrm{F^-}(aq) \tag{5.E.3}$$

5.E.3.41: Q14.3.29

Why is the hydronium ion concentration in a solution that is 0.10 *M* in HCl and 0.10 *M* in HCOOH determined by the concentration of HCl?

5.E.3.42: S14.3.29

This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the HCO_2H exists primarily as HCO_2H molecules because the ionization of the weak acid is suppressed by the strong acid. Therefore, the HCO_2H contributes a negligible amount of hydronium ions to the solution. The stronger acid, HCl, is the dominant producer of hydronium ions because it is completely ionized. In such a solution, the stronger acid determines the concentration of hydronium ions, and the ionization of the weaker acid is fixed by the $[H_3O^+]$ produced by the stronger acid.

5.E.3.43: Q14.3.30

From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

CH_3CO_2H: $[H_3O^+] = 1.34 \times 10^{-3}$ *M*;

$[CH_3CO_2^-] = 1.34 \times 10^{-3}$ *M*;

$[CH_3CO_2H] = 9.866 \times 10^{-2}$ *M*;

ClO^-: $[OH^-] = 4.0 \times 10^{-4}$ *M*;

$[HClO] = 2.38 \times 10^{-5}$ *M*;

$[ClO^-] = 0.273$ *M*;

HCO_2H: $[HCO_2H] = 0.524$ *M*;

$[H_3O^+] = 9.8 \times 10^{-3}$ *M*; $[HCO_2^-] = 9.8 \times 10^{-3}$ *M*;

$C_6H_5NH_3^+$: $[C_6H_5NH_3^+] = 0.233$ *M*;

$[C_6H_5NH_2] = 2.3 \times 10^{-3}$ *M*;

$[H_3O^+] = 2.3 \times 10^{-3}$ *M*

From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

NH_3: $[OH^-] = 3.1 \times 10^{-3}$ *M*;

$[NH_4^+] = 3.1 \times 10^{-3}$ *M*;

$[NH_3] = 0.533$ *M*;

HNO_2: $[H_3O^+] = 0.011$ *M*;

$[NO_2^-]$ = 0.0438 *M*;

$[HNO_2]$ = 1.07 *M*;

$(CH_3)_3N$: $[(CH_3)_3N]$ = 0.25 *M*;

$[(CH_3)_3NH^+]$ = 4.3 × 10^{-3} *M*;

$[OH^-]$ = 4.3 × 10^{-3} *M*;

NH_4^+ : $[NH_4^+]$ = 0.100 *M*;

$[NH_3]$ = 7.5 × 10^{-6} *M*;

$[H_3O^+]$ = 7.5 × 10^{-6} *M*

a. $K_b = 1.8 \times 10^{-5}$;
b. $K_a = 4.5 \times 10^{-4}$;
c. $K_b = 7.4 \times 10^{-5}$;
d. $K_a = 5.6 \times 10^{-10}$

5.E.3.44: Q14.3.31

Determine K_b for the nitrite ion, NO_2^-. In a 0.10-*M* solution this base is 0.0015% ionized.

5.E.3.45: Q14.3.32

Determine K_a for hydrogen sulfate ion, HSO_4^-. In a 0.10-*M* solution the acid is 29% ionized.

5.E.3.46: S14.3.32

$K_a = 1.2 \times 10^{-2}$

5.E.3.47: Q14.3.33

Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

a. F^-
b. NH_4^+
c. AsO_4^{3-}
d. $(CH_3)_2NH_2^+$
e. NO_2^-
f. $HC_2O_4^-$ (as a base)

5.E.3.48: Q14.3.52

Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

1. HTe^- (as a base)
2. $(CH_3)_3NH^+$
3. $HAsO_4^{3-}$ (as a base)
4. HO_2^- (as a base)
5. $C_6H_5NH_3^+$
6. HSO_3^- (as a base)

5.E.3.49: S14.3.52

a. $K_b = 4.3 \times 10^{-12}$;
b. $K_a = 1.4 \times 10^{-10}$;
c. $K_b = 1 \times 10^{-7}$;
d. $K_b = 4.2 \times 10^{-3}$;
e. $K_b = 4.2 \times 10^{-3}$;
f. $K_b = 8.3 \times 10^{-13}$

5.E.3.50: Q14.3.53

For which of the following solutions must we consider the ionization of water when calculating the pH or pOH?

a. 3×10^{-8} *M* HNO_3
b. 0.10 g HCl in 1.0 L of solution
c. 0.00080 g NaOH in 0.50 L of solution
d. 1×10^{-7} *M* $Ca(OH)_2$
e. 0.0245 *M* KNO_3

5.E.3.51: Q14.3.54

Even though both NH_3 and $C_6H_5NH_2$ are weak bases, NH_3 is a much stronger acid than $C_6H_5NH_2$. Which of the following is correct at equilibrium for a solution that is initially 0.10 *M* in NH_3 and 0.10 *M* in $C_6H_5NH_2$?

a. $[OH^-] = [NH_4^+]$
b. $[NH_4^+] = [C_6H_5NH_3^+]$
c. $[OH^-] = [C_6H_5NH_3^+]$
d. $[NH_3] = [C_6H_5NH_2]$
e. both a and b are correct

is the correct statement.

5.E.3.52: Q14.3.55

Calculate the equilibrium concentration of the nonionized acids and all ions in a solution that is 0.25 *M* in HCO_2H and 0.10 *M* in HClO.

5.E.3.53: Q14.3.56

Calculate the equilibrium concentration of the nonionized acids and all ions in a solution that is 0.134 *M* in HNO_2 and 0.120 *M* in HBrO.

5.E.3.54: S14.3.56

$[H_3O^+] = 7.5 \times 10^{-3}$ *M*

$[HNO_2] = 0.126$ $[OH^-] = 1.3 \times 10^{-12}$ *M* $[BrO^-] = 3.2 \times 10^{-8}$ *M* $[HBrO] = 0.120$ *M*

5.E.3.55: Q14.3.57

Calculate the equilibrium concentration of the nonionized bases and all ions in a solution that is 0.25 *M* in CH_3NH_2 and 0.10 *M* in C_5H_5N ($K_b = 1.7 \times 10^{-9}$).

5.E.3.56: Q14.3.58

Calculate the equilibrium concentration of the nonionized bases and all ions in a solution that is 0.115 *M* in NH_3 and 0.100 *M* in $C_6H_5NH_2$.

5.E.3.57: S14.3.58

$[OH^-] = [NO_4^+] = 0.0014$ *M*

$[NH_3] = 0.144$ *M* $[H_3O^+] = 6.9 \times 10^{-12}$ *M* $[C_6H_5NH_3^+] = 3.9 \times 10^{-8}$ *M* $[C_6H_5NH_2] = 0.100$ *M*

5.E.3.58: Q14.3.59

Using the K_a values in Appendix H, place $Al(H_2O)_6^{3+}$ in the correct location in Figure.

5.E.3.59: Q14.3.60

Calculate the concentration of all solute species in each of the following solutions of acids or bases. Assume that the ionization of water can be neglected, and show that the change in the initial concentrations can be neglected. Ionization constants can be found in Appendix H and Appendix I.

a. 0.0092 *M* HClO, a weak acid
b. 0.0784 *M* $C_6H_5NH_2$, a weak base

c. 0.0810 M HCN, a weak acid
d. 0.11 M $(CH_3)_3N$, a weak base
e. 0.120 M $Fe(H_2O)_6^{2+}$ a weak acid, $K_a = 1.6 \times 10^{-7}$

5.E.3.60: S14.3.60

$$\frac{[H_3O^+][ClO^-]}{[HClO]} = \frac{(x)(x)}{(0.0092 - x)} \approx \frac{(x)(x)}{0.0092} = 3.5 \times 10^{-8}$$

Solving for x gives 1.79×10^{-5} M. This value is less than 5% of 0.0092, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[H_3O^+] = [ClO] = 1.8 \times 10^{-5}$ $M$$[HClO] = 0.00092$ M $[OH^-] = 5.6 \times 10^{-10}$ M;

$$\frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} = \frac{(x)(x)}{(0.0784 - x)} \approx \frac{(x)(x)}{0.0784} = 4.6 \times 10^{-10}$$

Solving for x gives 6.01×10^{-6} M.

This value is less than 5% of 0.0784, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[CH_3CO_2^-]$ = $[OH^-]$ = 6.0×10^{-6} M $[C_6H_5NH_2]$ = 0.00784 $[H_3O^+]$ = 1.7×10^{-9} M; $\frac{[H_3O^+][CN^-]}{[HCN]} = \frac{(x)(x)}{(0.0810 - x)} \approx \frac{(x)(x)}{0.0810} = 4 \times 10^{-10}$ Solving for x gives 5.69×10^{-6} M. This value is less than 5% of 0.0810, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[H_3O^+]$ = $[CN^-] = 5.7 \times 10^{-6}$ M $[HCN] = 0.0810$ M $[OH^-] = 1.8 \times 10^{-9}$ M; $\frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{(0.11 - x)} \approx \frac{(x)(x)}{0.11} = 7.4 \times 10^{-5}$ Solving for x gives 2.85×10^{-3} M. This value is less than 5% of 0.11, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[(CH_3)_3NH^+] = [OH^-] = 2.9 \times 10^{-3}$ M $[(CH_3)_3N] = 0.11$ M $[H_3O^+] = 3.5 \times 10^{-12}$ M; $\frac{[Fe(H_2O)_5(OH)^+][H_3O^+]}{[Fe(H_2O)_6^{2+}]} = \frac{(x)(x)}{(0.120 - x)} \approx \frac{(x)(x)}{0.120} = 1.6 \times 10^{-7}$ Solving for x gives 1.39×10^{-4} M. This value is less than 5% of 0.120, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[Fe(H_2O)_5(OH)^+] = [H_3O^+] = 1.4 \times 10^{-4}$ M $[Fe(H_2O)_6^{2+}] = 0.120$ M $[OH^-] = 7.2 \times 10^{-11}$ M

5.E.3.61: Q14.3.61

Propionic acid, $C_2H_5CO_2H$ ($K_a = 1.34 \times 10^{-5}$), is used in the manufacture of calcium propionate, a food preservative. What is the hydronium ion concentration in a 0.698-M solution of $C_2H_5CO_2H$?

5.E.3.62: Q14.3.62

White vinegar is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is 1.007 g/cm^3, what is the pH?

5.E.3.63: S14.3.62

pH = 2.41

5.E.3.64: Q14.3.63

The ionization constant of lactic acid, $CH_3CH(OH)CO_2H$, an acid found in the blood after strenuous exercise, is 1.36×10^{-4}. If 20.0 g of lactic acid is used to make a solution with a volume of 1.00 L, what is the concentration of hydronium ion in the solution?

5.E.3.65: Q14.3.64

Nicotine, $C_{10}H_{14}N_2$, is a base that will accept two protons ($K_1 = 7 \times 10^{-7}$, $K_2 = 1.4 \times 10^{-11}$). What is the concentration of each species present in a 0.050-M solution of nicotine?

5.E.3.66: S14.3.64

$[C_{10}H_{14}N_2] = 0.049$ M

$[C_{10}H_{14}N_2H^+] = 1.9 \times 10^{-4}$ M $[C_{10}H_{14}N_2H_2^{2+}] = 1.4 \times 10^{-11}$ M $[OH^-] = 1.9 \times 10^{-4}$ M $[H_3O^+] = 5.3 \times 10^{-11}$ M

5.E.3.67: Q14.3.65

The pH of a 0.20-*M* solution of HF is 1.92. Determine K_a for HF from these data.

5.E.3.68: Q14.3.66

The pH of a 0.15-*M* solution of HSO_4^- is 1.43. Determine K_a for HSO_4^- from these data.

5.E.3.69: S14.3.66

$K_a = 1.2 \times 10^{-2}$

5.E.3.70: Q14.3.67

The pH of a 0.10-*M* solution of caffeine is 11.16. Determine K_b for caffeine from these data:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq)$$

5.E.3.71: Q14.3.68

The pH of a solution of household ammonia, a 0.950 M solution of $NH_{3,}$ is 11.612. Determine K_b for NH_3 from these data.

5.E.3.72: S14.3.68

$K_b = 1.77 \times 10^{-5}$

5.E.4: Hydrolysis of Salt Solutions

5.E.4.1: Q14.4.1

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. $Al(NO_3)_3$
b. RbI
c. $KHCO_2$
d. CH_3NH_3Br

5.E.4.2: Q14.4.2

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. $FeCl_3$
b. K_2CO_3
c. NH_4Br
d. $KClO_4$

5.E.4.3: S14.4.2

acidic; basic; acidic; neutral

5.E.4.4: Q14.4.3

Novocaine, $C_{13}H_{21}O_2N_2Cl$, is the salt of the base procaine and hydrochloric acid. The ionization constant for procaine is 7×10^{-6}. Is a solution of novocaine acidic or basic? What are $[H_3O^+]$, $[OH^-]$, and pH of a 2.0% solution by mass of novocaine, assuming that the density of the solution is 1.0 g/mL.

CHAPTER OVERVIEW

6: Acid-Base Equilibria in Mixtures

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6.1: Mixtures of Acids

In the previous chapter, we discussed solutions that contained only one acid or one base. In many cases, our solutions will contain a mixture of acids or bases. The equilibrium of each of the components of a system will affect the others if there are **common ions** between the equilibria. Here we discuss why common ions are important to consider for equilibrium systems, and then present strategies to determine the pH of a solution with a mixture of acids or bases.

Common Ion Effect

Consider a solution that contains both hydrochloric acid and acetic acid. Because hydrochloric acid is considered a strong acid, we expect that it will ionize completely to form hydronium ions and chloride ions.

$$\mathrm{HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-} \tag{6.1.1}$$

Acetic acid is considered a weak acid and so will only partially ionize, as shown here.

$$\mathrm{HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-} \tag{6.1.2}$$

The extent of ionization will depend on the Ka for acetic acid, 1.8 x 10^{-5}, and on the concentrations of the reactant and product species. According to Le Chatelier's principle, if we increase $[\mathrm{HC_2H_3O_2}]$, the equilibrium will shift to the right, increasing $[\mathrm{H_3O^+}]$ and decreasing the pH. If we increase the concentration of either product, the equilibrium will shift to the left and more $\mathrm{H_2C_3O_2}$ will exist in solution at equilibrium.

When multiple acids are present in a solution, the hydronium resulting from each ionization may affect other ionizations. This is termed the **common ion effect**.

Mixtures of Acids

When a solution contains a mixture of acids, the pH of the solution will be dominated by the stronger acid. Let's consider again the solution containing both HCl and $[\mathrm{HC_2H_3O_2}]$. If each of these acids were present at a concentration of 0.10 M, how could we determine the pH of the solution? We know that the HCl is a much stronger acid and so it will contribute the vast majority of hydronium ions to the solution. In this case, because HCl is strong, we expect $[\mathrm{H_3O^+}]$ from the HCl to be equal to its concentration, 0.10 M. To find the amount of hydronium contributed by the acetic acid, we can use an ICE table. However, unlike in the previous chapter, in this scenario the initial concentration of the hydronium, $[\mathrm{H_3O^+}]_0$, is 0.10 M - or the amount resulting from ionization of the HCl.

	$\mathrm{HC_2H_3O_2(aq)+}$	$\mathrm{H_2O(l)} \rightleftharpoons$	$\mathrm{H_3O^+(aq)+}$	$\mathrm{C_2H_3O_2-(aq)}$
Initial	0.10 M	excess	0.10 M	0
Change	-x	-x	+x	+x
Equilibrium	(0.10 - x)	excess	(0.10 + x)	x

Solving for x in the ICE table:

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{C_2H_3O_2-}]}{[\mathrm{HC_2H_3O_2}]} = 1.8 \times 10^{-5} \tag{6.1.3}$$

$$K_a = \frac{(0 \cdot 10 + \mathrm{x})(\mathrm{x})}{(0 \cdot 10 - \mathrm{x})} = 1.8 \times 10^{-5} \tag{6.1.4}$$

$$x = 1.8 \times 10^{-5} \tag{6.1.5}$$

$$[\mathrm{H_3O^+}] = (0.10 + x) \approx 0.10M \tag{6.1.6}$$

In this case, the acetic acid contributed such a small amount of hydronium to the solution that it did not contribute significantly to the overall concentration (i.e. 0.10 M). This behavior is often seen in mixtures of acids. When two acids are mixed, if one acid is much stronger than the other (e.g. the $\mathrm{K_a}$ values differ by at least 1000-fold), the weaker acid does not contribute significantly to the equilibrium $[\mathrm{H_3O^+}]$ and can be ignored.

✓ Example 6.1.1 pH for a solution with HF and HBrO

What is the pH of a solution that contains $0.120\ M$ HF and $0.250\ M$ HBrO?

Solution

First we must determine which acid will contribute more protons to the solution by comparing the K_a values.

$K_a\ for\ \mathrm{HF} = 3.5 \times 10^{-4}$

$K_a\ for\ \mathrm{HBrO} = 2.8 \times 10^{-9}$

Because **HF** is much stronger, its hydronium contribution will dominate the pH. Because the Ka values differ by more than 1000-fold we can ignore the contribution from HBrO.

	$\mathrm{HF(aq)} +$	$\mathrm{H_2O(l)} \rightleftharpoons$	$\mathrm{H_3O^+(aq)} +$	$\mathrm{F^-(aq)}$
Initial	0.120 M	excess	~ 0	0
Change	-x	-x	+x	+x
Equilibrium	(0.120 - x)	excess	x	x

Solving for x,

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{F^-}]}{[\mathrm{HF}]} = 3.5 \times 10^{-4} \tag{6.1.7}$$

$$K_a = \frac{(\mathrm{x})(\mathrm{x})}{(0 \cdot 120 - \mathrm{x})} = 3.5 \times 10^{-4} \tag{6.1.8}$$

$$x = [\mathrm{H_3O^+}] = 6.5 \times 10^{-3} \tag{6.1.9}$$

$$pH = -log([\mathrm{H_3O^+}]) = -log(6.5 \times 10^{-3}) = 2.19 \tag{6.1.10}$$

? Exercise 6.1.1

What is the pH of a mixture of 0.25 M HCN and 0.025 M $\mathrm{HNO_3}$?

Answer

In this mixture, the $\mathrm{HNO_3}$ is the stronger acid. It is one of the strong acids so it ionizes completely, resulting in $[\mathrm{H_3O^+}] = 0.025\ M$. The HCN is much weaker with a K_a value of 4.9×10^{-10}. Its contribution to the pH can be ignored.

$$pH = -log[\mathrm{H_3O^+}] = -log(0.025) \tag{6.1.11}$$

$$pH = 1.60 \tag{6.1.12}$$

Mixtures of Bases

Similar to acids, when a solution contains a mixture of bases, the pH will be dominated by the stronger base.

? Exercise 6.1.2

You titrate a solution of HF with NaOH. The final concentration NaOH is 0.014 M and the final concentration of $\mathrm{F^-}$ is 0.125 M. What is the pH of the solution?

Answer

In this mixture, the NaOH is the stronger base. The $\mathrm{F^-}$ is much weaker with a K_b value of 2.9×10^{-11}. Its contribution to the pH can be ignored.

$$[\mathrm{OH^-}] = 0.014\ M \tag{6.1.13}$$

$$pOH = -log[\mathrm{OH^-}] = -log(0.014) = 1.85 \tag{6.1.14}$$

$$pH = 14.00 - 1.85 = 12.15 \tag{6.1.15}$$

Summary

When a solution contains a mixture of acids or bases, the strongest acid or base will contribute the most to the equilibrium \(\ce{[H3O^+]}. If the Ka (or Kb) values of multiple acids (or bases) differ by more than 1000-fold, the contribution of the weaker component can be ignored.

6.2: Polyprotic Acids

Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton
- Predict whether amphoteric species will act as acids or bases in solution and calculate the pH of a solution

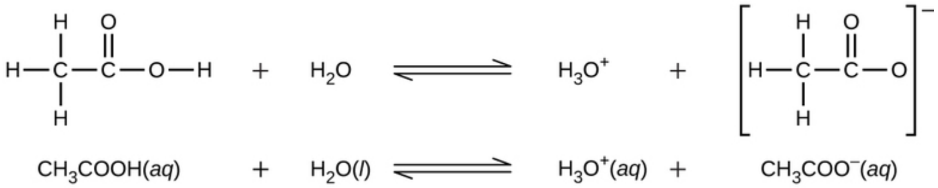
We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, HNO_3, and HCN that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq) \tag{6.2.1}$$

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq) \tag{6.2.2}$$

$$HCN(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CN^-(aq) \tag{6.2.3}$$

Even though it contains four hydrogen atoms, acetic acid, CH_3CO_2H, is also monoprotic because only the hydrogen atom from the carboxyl group ($-COOH$) reacts with bases:



Similarly, monoprotic bases are bases that will accept a single proton.

6.2.1: 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**

$$H_2SO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_4^-(aq) \tag{6.2.4}$$

with $K_{a1} > 10^2;\ complete\ dissociation$.

- **The second ionization is**

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \tag{6.2.5}$$

with $K_{a2} = 1.2 \times 10^{-2}$.

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, 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**

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \tag{6.2.6}$$

with

$$K_{H_2CO_3} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7} \tag{6.2.7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

- **Second Ionization**

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \tag{6.2.8}$$

with

$$K_{HCO_3^-} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = 4.7 \times 10^{-11} \tag{6.2.9}$$

$K_{H_2CO_3}$ is larger than $K_{HCO_3^-}$ 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 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 HCO_3^- are practically equal in a pure aqueous solution of H_2CO_3.

The sequential Ka values for a polyprotic acid are labeled K_{a1}, K_{a2}, K_{a3}, etc., and refer respectively to the acid ionization constant for the proton that ionizes first, the proton that ionizes next, and so on.

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 6.2.1: 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 $[H_3O^+]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ in a saturated solution of CO_2 with an initial $[H_2CO_3]$ = 0.033 *M*?

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_{a1} = 4.3 \times 10^{-7} \qquad \text{(equilibrium step 1)}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \quad K_{a2} = 4.7 \times 10^{-11} \qquad \text{(equilibrium step 2)}$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than HCO_3^-, so H_2CO_3 is the dominant producer of hydronium ion in solution. Thus there are two parts in the solution of this problem:

1. First Ionization: Determine the concentrations of \(\ce{H3O+}\) *and* \(\ce{HCO3-}\).

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).

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_{a1} = 4.3 \times 10^{-7}$$

An abbreviated table of changes and concentrations shows:

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:

$$[H_2CO_3] = 0.033\ M$$

$$[\mathrm{H_3O^+}] = [\mathrm{HCO_3^-}] = 1.2 \times 10^{-4}\ M$$

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:

$$\mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CO_3^{2-}}(aq)$$

ICE Table	$\mathrm{HCO_3^-}(aq)$	$\mathrm{H_2O}(l)$	$\mathrm{H_3O^+}(aq)$	$\mathrm{CO_3^{2-}}(aq)$
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

$$\begin{aligned} K_{\mathrm{HCO_3^-}} &= \frac{[\mathrm{H_3O^+}][\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]} \\ &= \frac{(1.2 \times 10^{-4}\ M + y)(y)}{(1.2 \times 10^{-4}\ M - y)} \end{aligned}$$

We can assume $y \ll 1.2 \times 10^{-4}\ M$ so

$$K_{\mathrm{HCO_3^-}} = 4.7 \times 10^{-11} \approx \frac{(1.2 \times 10^{-4}\ M)(y)}{(1.2 \times 10^{-4}\ M)}$$

$$[\mathrm{CO_3^{2-}}] = y \approx 4.7 \times 10^{-11}$$

? Exercise 6.2.2: 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:

$$\mathrm{H_2S}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HS^-}(aq) \quad K_{\mathrm{a1}} = 8.9 \times 10^{-8}$$

$$\mathrm{HS^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{S^{2-}}(aq) \quad K_{\mathrm{a2}} = 1.0 \times 10^{-19}$$

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).

6.2.2: 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**

$$\mathrm{H_3PO_4}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{H_2PO_4^-}(aq) \tag{6.2.10}$$

with $K_{\mathrm{a1}} = 7.5 \times 10^{-3}$.

- **The second ionization is**

$$\mathrm{H_2PO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HPO_4^{2-}}(aq) \tag{6.2.11}$$

with $K_{\mathrm{a2}} = 6.2 \times 10^{-8}$.

- **The third ionization is**

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq) \tag{6.2.12}$$

with $K_{a3} = 4.2 \times 10^{-13}$.

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 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:

$$H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + OH^-(aq) \tag{6.2.13}$$

and

$$H_2O(l) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) + OH^-(aq) \tag{6.2.14}$$

6.2.3: Polyprotic Acids Contain Amphoteric Species

Because polyprotic acids contain more than one ionizable proton, the conjugate bases of polyprotic acids are amphoteric species - species that can either accept or donate a proton. When an amphoteric species exists in solution, it has the ability to act as either an acid or a base. For example, bicarbonate participates in the following equilibria:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \tag{6.2.15}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq) \quad K_b = 2.3 \times 10^{-8} \tag{6.2.16}$$

Which of these equilibrium reactions dominates the pH of the solution depends on the relative magnitudes of the K_a and K_b values.

Typically we are only given the K_a values for the ionizable protons of the polyprotic acid. We can use the K_a for the ionization of the proton in question to determine the K_b for the base reaction.

The acid equilibrium reaction here represents the ionization of the second proton from H_2CO_3, thus the acid ionization constant is K_{a2}.

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \quad K_{a2} = 4.7 \times 10^{-11} \tag{6.2.17}$$

The base equilibrium reaction here represents re-association of the first proton from H_2CO_3. To calculate the K_b for this reaction, we will use K_{a1}:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_{a1} = 4.3 \times 10^{-7} \tag{6.2.18}$$

$$K_b = \frac{K_w}{K_{a1}} = \frac{1 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8} \tag{6.2.19}$$

In this case, K_b (2.3×10^{-8}) is much larger than K_a (4.7×10^{-11}) so the bicarbonate will act as a base in solution.

✓ Example 6.2.2 pH of a solution with an amphoteric species

What is the pH of a solution that contains 0.20 M $NaHSO_3$?

Solution

In this solution, the Na+ is pH neutral. The HSO_3^- can act as either an acid or a base. The acid equilibrium reaction and Ka value are:

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_3^{2-}(aq) \quad K_{a2} = 6.4 \times 10^{-8} \tag{6.2.20}$$

The base equilibrium reaction is:

$$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_2SO_3(aq) + OH^-(aq) \tag{6.2.21}$$

To determine the K_b, we can use the K_a for sulfurous acid, $K_{a1} = 1.7 \times 10^{-2}$.

$$K_b = \frac{K_w}{K_{a1}} = \frac{1 \times 10^{-14}}{1.7 \times 10^{-2}} = 5.9 \times 10^{-13} \tag{6.2.22}$$

The acid equilibrium reaction will dominate the pH of the solution.

	$\mathrm{HSO_3^-(aq)}+$	$\mathrm{H_2O(l)} \rightleftharpoons$	$\mathrm{H_3O^+(aq)}+$	$\mathrm{SO_3^{2-}(aq)}$
Initial	0.20 M	excess	~ 0	0
Change	-x	-x	+x	+x
Equilibrium	(0.20 - x)	excess	x	x

Solving for x,

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{SO_3^{2-}}]}{[\mathrm{HSO_3^-}]} = 6.4 \times 10^{-8} \tag{6.2.23}$$

$$K_a = \frac{\mathrm{(x)(x)}}{\mathrm{(0 \cdot 20 - x)}} = 6.4 \times 10^{-8} \tag{6.2.24}$$

$$x = [\mathrm{H_3O^+}] = 1.1 \times 10^{-4} \tag{6.2.25}$$

$$pH = -log([\mathrm{H_3O^+}]) = -log(1.1 \times 10^{-4}) = 3.95 \tag{6.2.26}$$

? Exercise 6.2.3

What is the pH of a solution that contains 0.100 M K_2HPO_4? (K_a values are provided above.)

Answer

The $\mathrm{K^+}$ ion is pH neutral, so we need only to focus on the equilibrium reactions for $\mathrm{HPO_4^{2-}}$.

The $\mathrm{HPO_4^{2-}}$ ion can act as an acid as follows:

$$\mathrm{HPO_4^{2-}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{PO_4^{3-}}(aq) \quad K_{a3} = 4.2 \times 10^{-13} \tag{6.2.27}$$

The $\mathrm{HPO_4^{2-}}$ ion can act as a base as follows:

$$\mathrm{HPO_4^{2-}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2PO_4^-}(aq) + \mathrm{OH^-}(aq) \tag{6.2.28}$$

The K_b for this reaction is calculated using K_{a2}:

$$K_b = \frac{1 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7} \tag{6.2.29}$$

In this case, K_b is much larger than K_a and the species predominately acts as a base.

pH = 10.10

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

6.3: Buffers

Learning Objectives

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

A mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) is called a buffer solution, or a buffer. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure 6.3.1). A solution of acetic acid (CH_3COOH and sodium acetate CH_3COONa) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia ($NH_3(aq)$) and ammonium chloride ($NH_4Cl(aq)$).

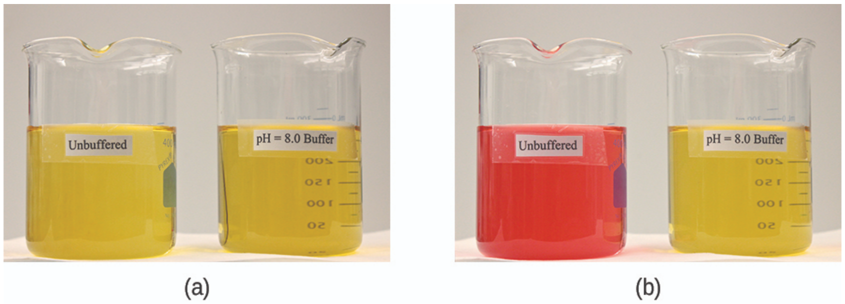


Figure 6.3.1: (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-M HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

6.3.1: How Buffers Work

A mixture of acetic acid and sodium acetate is acidic because the K_a of acetic acid is greater than the K_b of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value:

$$CH_3CO_2H(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CH_3CO_2^-(aq) \tag{6.3.1}$$

The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:

$$H_3O^+(aq) + CH_3CO_2^-(aq) \longrightarrow CH_3CO_2H(aq) + H_2O(l) \tag{6.3.2}$$

Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (Figure 6.3.2).

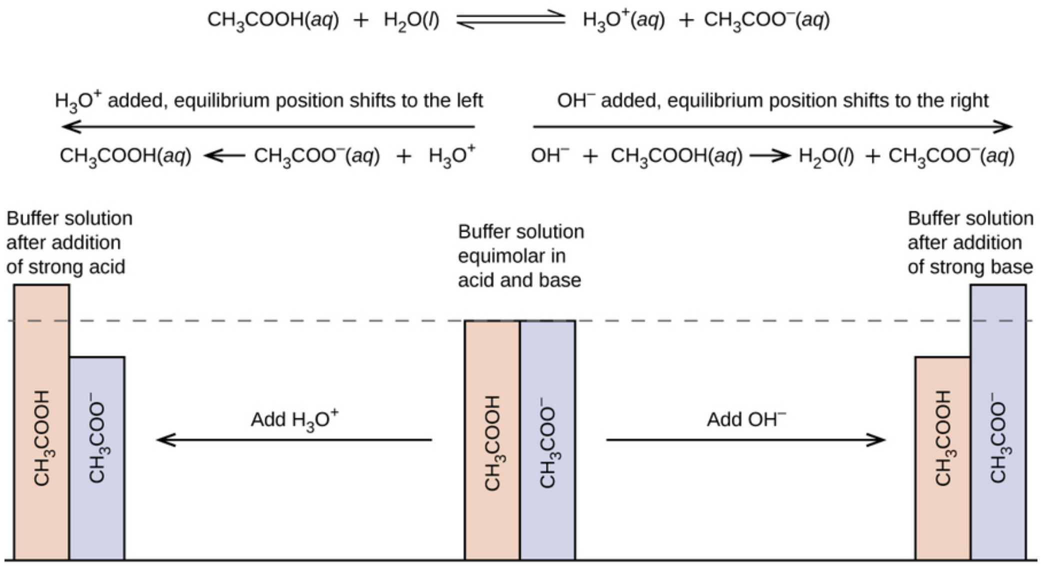


Figure 6.3.2: This diagram shows the buffer action of these reactions.

A mixture of ammonia and ammonium chloride is basic because the K_b for ammonia is greater than the K_a for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:

$$\mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \tag{6.3.3}$$

If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

$$\mathrm{H_3O^+}(aq) + \mathrm{NH_3}(aq) \longrightarrow \mathrm{NH_4^+}(aq) + \mathrm{H_2O}(l) \tag{6.3.4}$$

The three parts of the following example illustrate the change in pH that accompanies the addition of base to a buffered solution of a weak acid and to an unbuffered solution of a strong acid.

✓ Example 6.3.1: pH Changes in Buffered and Unbuffered Solutions

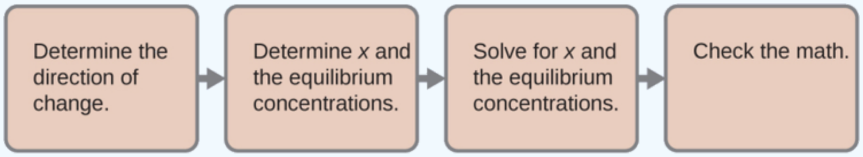
Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might change the biochemical activity of these compounds.

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.
b. Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

Solution

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.

To determine the pH of the buffer solution we use a typical equilibrium calculation (as illustrated in earlier Examples):



1. *Determine the direction of change.* The equilibrium in a mixture of H_3O^+, $CH_3CO_2^-$, and CH_3CO_2H is:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \tag{6.3.5}$$

The equilibrium constant for CH_3CO_2H is not given, so we look it up in Table E1: $K_a = 1.8 \times 10^{-5}$. With $[CH_3CO_2H] = [CH_3CO_2^-] = 0.10\ M$ and $[H_3O^+] = \sim 0\ M$, the reaction shifts to the right to form H_3O^+.

2. *Determine* x *and equilibrium concentrations.* A table of changes and concentrations follows:

	$[CH_3CO_2H] + [H_2O] \rightleftharpoons H_3O^+ + [CH_3CO_2^-]$		
Initial concentration (*M*)	0.10	~0	0.10
Change (*M*)	$-x$	x	x
Equilibrium constant (*M*)	$0.10 - x$	x	$0.10 + x$

3. *Solve for x and the equilibrium concentrations.* We find:

$$x = 1.8 \times 10^{-5}\ M \tag{6.3.6}$$

and

$$[H_3O^+] = 0 + x = 1.8 \times 10^{-5}\ M \tag{6.3.7}$$

Thus:

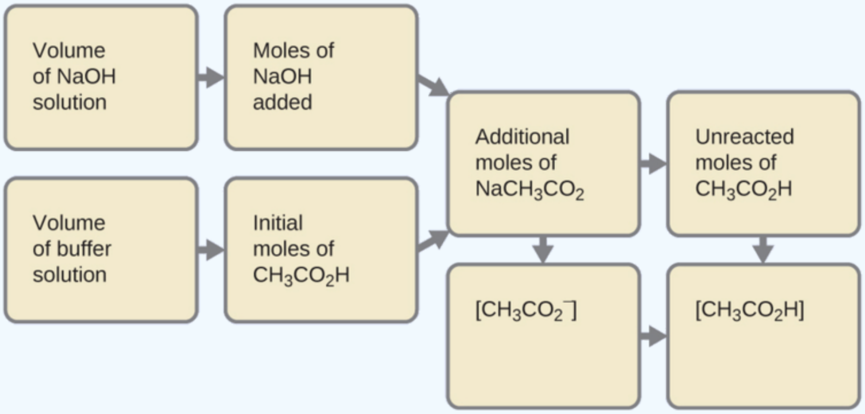
$$pH = -\log[H_3O^+] = -\log(1.8 \times 10^{-5}) \tag{6.3.8}$$

$$= 4.74 \tag{6.3.9}$$

4. *Check the work.* If we calculate all calculated equilibrium concentrations, we find that the equilibrium value of the reaction coefficient, $Q = K_a$.

(b) Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

First, we calculate the concentrations of an intermediate mixture resulting from the complete reaction between the acid in the buffer and the added base. Then we determine the concentrations of the mixture at the new equilibrium:



1. *Determine the moles of NaOH.* One milliliter (0.0010 L) of 0.10 *M* NaOH contains:

$$0.0010\ \cancel{L} \times \left(\frac{0.10\ \text{mol NaOH}}{1\ \cancel{L}}\right) = 1.0 \times 10^{-4}\ \text{mol NaOH} \tag{6.3.10}$$

2. *Determine the moles of CH_2CO_2H.* Before reaction, 0.100 L of the buffer solution contains:

$$0.100\ \cancel{L} \times \left(\frac{0.100\ \text{mol } CH_3CO_2H}{1\ \cancel{L}}\right) = 1.00 \times 10^{-2}\ \text{mol } CH_3CO_2H \tag{6.3.11}$$

3. *Solve for the amount of $NaCH_3CO_2$ produced.* The 1.0 × 10^{-4} mol of NaOH neutralizes 1.0 × 10^{-4} mol of CH_3CO_2H, leaving:

$$(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2}\ \text{mol } CH_3CO_2H \tag{6.3.12}$$

and producing 1.0 × 10^{-4} mol of $NaCH_3CO_2$. This makes a total of:

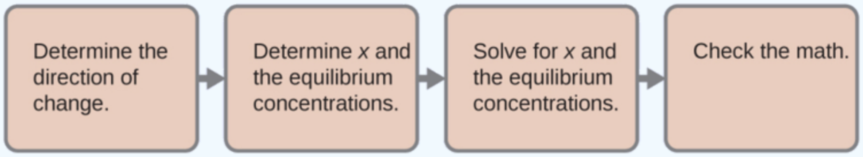
[\mathrm{(1.0×10^{−2})+(0.01×10^{−2})=1.01×10^{−2}\:mol\:NaCH_3CO_2} \]

4. *Find the molarity of the products.* After reaction, CH_3CO_2H and $NaCH_3CO_2$ are contained in 101 mL of the intermediate solution, so:

$$[CH_3CO_2H] = \frac{9.9 \times 10^{-3}\ \text{mol}}{0.101\ \text{L}} = 0.098\ M \tag{6.3.13}$$

$$[\mathrm{NaCH_3CO_2}] = \frac{1.01 \times 10^{-2}\ \mathrm{mol}}{0.101\ \mathrm{L}} = 0.100\ M \tag{6.3.14}$$

Now we calculate the pH after the intermediate solution, which is 0.098 M in CH_3CO_2H and 0.100 M in $NaCH_3CO_2$, comes to equilibrium. The calculation is very similar to that in part (a) of this example:



This series of calculations gives a pH = 4.75. Thus the addition of the base barely changes the pH of the solution.

(c) For comparison, calculate the pH after 1.0 mL of 0.10 M NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74 (a 1.8×10^{-5}-M solution of HCl). The volume of the final solution is 101 mL.

Solution

This 1.8×10^{-5}-M solution of HCl has the same hydronium ion concentration as the 0.10-M solution of acetic acid-sodium acetate buffer described in part (a) of this example. The solution contains:

$$0.100\ \mathrm{L} \times \left(\frac{1.8 \times 10^{-5}\ \mathrm{mol\ HCl}}{1\ \mathrm{L}}\right) = 1.8 \times 10^{-6}\ \mathrm{mol\ HCl}$$

As shown in part (b), 1 mL of 0.10 M NaOH contains 1.0×10^{-4} mol of NaOH. When the NaOH and HCl solutions are mixed, the HCl is the limiting reagent in the reaction. All of the HCl reacts, and the amount of NaOH that remains is:

$$(1.0 \times 10^{-4}) - (1.8 \times 10^{-6}) = 9.8 \times 10^{-5}\ M$$

The concentration of NaOH is:

$$\frac{9.8 \times 10^{-5}\ M\ \mathrm{NaOH}}{0.101\ \mathrm{L}} = 9.7 \times 10^{-4}\ M$$

The pOH of this solution is:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(9.7 \times 10^{-4}) = 3.01$$

The pH is:

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 10.99$$

The pH changes from 4.74 to 10.99 in this unbuffered solution. This compares to the change of 4.74 to 4.75 that occurred when the same amount of NaOH was added to the buffered solution described in part (b).

? Exercise 6.3.1

Show that adding 1.0 mL of 0.10 M HCl changes the pH of 100 mL of a 1.8×10^{-5} M HCl solution from 4.74 to 3.00.

Answer

Initial pH of 1.8×10^{-5} M HCl; pH = $-\log[H_3O^+] = -\log[1.8 \times 10^{-5}] = 4.74$

Moles of H_3O^+ added by addition of 1.0 mL of 0.10 M HCl: 0.10 moles/L × 0.0010 L = 1.0×10^{-4} moles; final pH after addition of 1.0 mL of 0.10 M HCl:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log\left(\frac{\text{total moles } \mathrm{H_3O^+}}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4}\ \mathrm{mol} + 1.8 \times 10^{-6}\ \mathrm{mol}}{101\ \mathrm{mL}\left(\frac{1\ \mathrm{L}}{1000\ \mathrm{mL}}\right)}\right) = 3.00 \tag{6.3.15}$$

6.3.2: Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 6.3.3). If we add so much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion.

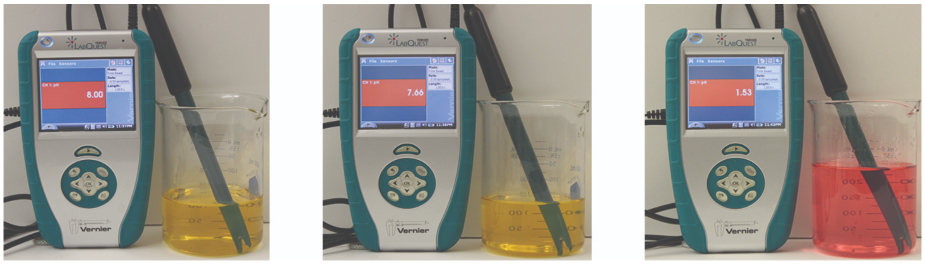


Figure $6.3.3$: The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The buffer capacity is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 M in acetic acid and 1.0 M in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 M in acetic acid and 0.10 M in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

6.3.3: Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. Figure $6.3.4$ shows an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

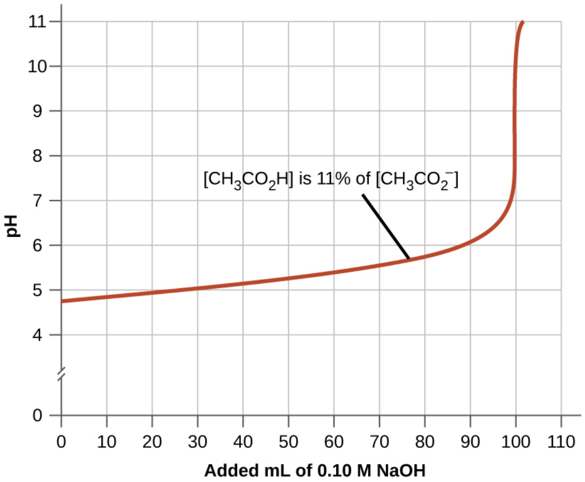


Figure $6.3.4$: The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially, $[\mathrm{CH_3CO_2H}] = 0.10\ M$ and $[\mathrm{CH_3CO_2^-}] = 0.10\ M$.

2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, H_2CO_3, and the bicarbonate ion, HCO_3^-. When an excess of hydrogen ion enters the blood stream, it is removed primarily by the reaction:

$$\mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \longrightarrow \mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \tag{6.3.16}$$

When an excess of the hydroxide ion is present, it is removed by the reaction:

$$\mathrm{OH^-}(aq) + \mathrm{H_2CO_3}(aq) \longrightarrow \mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l) \tag{6.3.17}$$

The pH of human blood thus remains very near 7.35, that is, slightly basic. Variations are usually less than 0.1 of a pH unit. A change of 0.4 of a pH unit is likely to be fatal.

6.3.4: Summary

A solution containing a mixture of an acid and its conjugate base, or of a base and its conjugate acid, is called a buffer solution. Unlike in the case of an acid, base, or salt solution, the hydronium ion concentration of a buffer solution does not change greatly when a small amount of acid or base is added to the buffer solution. The base (or acid) in the buffer reacts with the added acid (or base).

6.3.5: Key Equations

- $pK_a = -\log K_a$
- $pK_b = -\log K_b$

Glossary

buffer capacity

amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

buffer

mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

Henderson-Hasselbalch equation

equation used to calculate the pH of buffer solutions

6.4: Henderson-Hasselbalch Approximation

Learning Objectives

- To calculate the pH of a buffer solution
- To calculate the pH of a buffer solution after the addition of a strong acid or base

We have straightforward calculations for strong acids and bases, but the computations behind buffers are rather complex and time consuming. The **Henderson-Hasselbalch approximation** use the fact that weak acids and bases barely ionize, allowing us to approximate the pH of buffer solutions using initial concentrations. Though the approximation has a few restrictions, it simplifies a lengthy calculation into a simple equation derived from K. The basic equation is as follows:

$$pH \approx pK_a + \log_{10} \frac{[A^-]}{[HA]} \tag{6.4.1}$$

This equation uses the **pKa** of the acid rather than the Ka. The pKa and the Ka for a given acid are related by the p-function:

$$pK_a = -log(K_a) \tag{6.4.2}$$

$$K_a = 10^{-pK_a} \tag{6.4.3}$$

Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878-1942) was a talented biochemist, among many other titles, who spent most of his career at Harvard. He was responsible for developing the components of the equation after studying equilibrium reactions that took place within blood as a result of respiration (specializing in "fatigue"). His equation was incomplete without the solid calculations into it provided by Hasselbalch.

Karl Albert Hasselbalch (1874-1962) was a chemist who studied pH closely. He also studied blood and reactions that took place with oxygen, to put in the simplest of terms. He eventually modified Henderson's equation by putting mathematical *logs* into it creating a solid relationship.

Derivation for Buffers from Weak Acids

For a weak acid HA and its conjugate base A^-:

$$HA + H_2O \rightleftharpoons H^+ + A^-$$

which has an acid ionization constant K_a. The Henderson-Hasselbalch approximation is derived from this acid ionization constant.

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{6.4.4}$$

$$-\log_{10} K_a = -\log_{10} \frac{[H^+][A^-]}{[HA]} \tag{6.4.5}$$

$$-\log_{10} K_a = -\log_{10}[H^+] - \log_{10} \frac{[A^-]}{[HA]} \tag{6.4.6}$$

$$pK_a = pH - \log_{10} \frac{[A^-]}{[HA]} \tag{6.4.7}$$

$$pH = pK_a + \log_{10} \frac{[A^-]}{[HA]} \tag{6.4.8}$$

pH Calculations for Buffer Solutions

Equation 6.4.8 is formulated in terms of equilibrium concentrations in solution. Since HA is a weak acid and weakly dissociates and we can introduce two approximations

$$[HA] \approx [HA]_i \tag{6.4.9}$$

and

$$[A^-] \approx [A^-]_i \tag{6.4.10}$$

Hence, we can use the initial concentrations rather than equilibrium concentrations because

$$pK_a + \log_{10}\frac{[A^-]_i}{[HA]_i} \approx pK_a + \log_{10}\frac{[A^-]}{[HA]} = pH \tag{6.4.11}$$

✓ Example 6.4.1: Nitrous acid buffer

Find $[\mathrm{H_3O^+}]$ in a solution of 1.0 M HNO_2 and 0.225 M $NaNO_2$. The K_a for HNO_2 is 5.6×10^{-4}.

Solution

$$pK_a = -\log_{10} K_a = -\log_{10}(7.4 \times 10^{-4}) = 3.14$$

$$pH = pK_a + \log_{10}\left(\frac{[NO_2^-]}{[HNO_2]}\right)$$

$$pH = 3.14 + \log_{10}\left(\frac{1}{0.225}\right)$$

$$pH = 3.14 + 0.648 = 3.788$$

$$[H^+] = 10^{-pH} = 10^{-3.788} = 1.6 \times 10^{-4}$$

? Exercise 6.4.1

How many grams of sodium acetate $\mathrm{NaC_2H_3O_2}$ should be added to 1.0 L of a 1.0 M $\mathrm{HC_2H_3O_2}$ solution to prepare a buffer of pH 5.0? (K_a acetic acid is 1.75×10^{-5}.

Answer

$$pKa = -logKa = -log(1.8 \times 10^{-5}) = 4.74$$

$$pH = pK_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

$$5.0 = 4.74 + \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

$$0.26 = \log_{10}\left(\frac{[A^-]}{[HA]}\right)$$

$$10^{0.26} = \frac{[A^-]}{[HA]}$$

$$1.8 = \frac{[A^-]}{[HA]}$$

The solution should have 1.8 times as much acetate compared to acetic acid to achieve a pH of 5.0. In 1.0 L, we need 1.8 mole $\mathrm{NaC_2H_3O_2}$.

$$1.8\ mol\ \mathrm{NaC_2H_3O_2} \times \frac{82.04\ g\ \mathrm{NaC_2H_3O_2}}{1\ mol\ \mathrm{NaC_2H_3O_2}} = 150\ g\ \mathrm{NaC_2H_3O_2} \tag{6.4.12}$$

The Henderson-Hasselbalch equation is written in terms of an acid, HA, and its conjugate base. But it can also be used to approximate the pH of a buffer solution prepared from a weak base. In this case, we simply calculate the K_a value from the K_b.

Exercise 6.4.2

You prepare a buffer solution of 0.323 M NH_3 and $(NH_4)_2SO_4$. What molarity of $(NH_4)_2SO_4$ is necessary to have a pH of 8.6? The pK_b for NH_3 is 4.74.

Answer

$$\begin{gathered} pK_a + pK_b = 14 \\ pK_a = 14 - 4.74 = 9.26 \\ pH = pK_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right) \\ 8.6 = 9.26 + \log_{10}\left(\frac{0.323}{[NH_4^+]}\right) \\ -0.66 = \log_{10}\left(\frac{0.323}{[NH_4^+]}\right) \\ [NH_4^+] = 1.48M \\ [\mathrm{(NH_4)_2SO_4}] = \frac{1.48}{2} = 0.74\ M \end{gathered} \tag{6.4.13}$$

Buffer Challenges

In practice, buffers are used to resist pH change in a reaction system. We anticipate that some amount of strong acid or strong base will be added to a buffer system. We call this "challenging the buffer". To calculate the pH of a solution after a buffer challenge, we use a two step procedure.

Step 1 - Determine the moles of HA and moles of A^- that remain following the addition of strong acid or base.

When a strong acid is added to a buffer solution, we can approximate that it will react completely with the base component of the buffer, A^-, to form the acid component, HA. When a strong base is added to a buffer solution, we can approximate that it will react completely with the acid component of the buffer, HA, to form the base component, A^-. The first step is to use stoichiometry to determine the amount of HA and A^- that remain in solution after the strong acid or strong base addition.

Step 2 - Determine the pH of the buffer using the Henderson-Hasselbalch approximation.

Buffer solutions will resist pH change, but they will not prevent it. The next step is to calculate the pH of the buffer solution using the new concentrations that you calculated in Step 1. Note that for a buffer solution, the molar amounts can also be used in the Henderson-Hasselbalch equation since the volume of the buffer solution is the same for HA and for A^-.

✓ Example 6.4.2: Buffering Capability

What is the pH of a buffer 0.500 moles acetic acid and 0.500 moles acetate ion and the total volume is 5 L when you add 0.035 moles HCl? The K_a for acetic acid is 1.75×10^{-5}.

Solution

Step 1. Determine the moles of acetic acid and moles of acetate.

HCl is an acid and will react with the basic component of the buffer:

$$\mathrm{HCl(aq) + C_2H_3O_2^-(aq) \rightarrow Cl^-(aq) + HC_2H_3O_2(aq)} \tag{6.4.14}$$

$$mol\ \mathrm{HC_2H_3O_2} = 0.500\ mol\ +\ 0.035\ mol\ =\ 0.535\ mol \tag{6.4.15}$$

$$[\mathrm{HC_2H_3O_2}]\ = \frac{0.535\ mol\ \mathrm{HC_2H_3O_2}}{5\ L\ solution} = 0.107\ M \tag{6.4.16}$$

$$mol\ \mathrm{C_2H_3O_2^-} = 0.500\ mol\ -\ 0.035\ mol\ =\ 0.465\ mol \tag{6.4.17}$$

$$[\mathrm{C_2H_3O_2^-}] = \frac{0.465\ mol\ \mathrm{C_2H_3O_2^-}}{5\ L\ solution} = 0.093\ M \tag{6.4.18}$$

Step 2. Determine the pH of the resulting buffer solution.

$$pK_a = -\log_{10} K_a = -\log_{10}(1.75 \times 10^{-5}) = 4.756$$

$$pH = pK_a + \log_{10}\left(\frac{[\mathrm{C_2H_3O_2^-}]}{[\mathrm{HC_2H_3O_2}]}\right)$$

$$pH = 4.756 + \log_{10}(0.869)$$

$$pH = 4.756 - 0.061 = 4.70$$

✓ Example 6.4.3: effective buffer range

What is the range of an acetic acid buffer described in problem 6.4.4 without the added HCl?

Solution

The effective buffer range is of magnitude 2 pH units with the pK_a as the midpoint.

$$pK_a = -\log_{10} K_a = -\log_{10}(1.75 \times 10^{-5}) = 4.756$$

Hence, the buffer range would be **3.75 to 5.75**.

References

1. "Henderson-Hasselbalch Equation: Its History and Limitations," Henry N. Po and N. M. Senozan, *J. Chem. Educ.*, 2001, 78 (11), p 1499
2. National Academy of Sciences (U.S.) Biographical memoirs. City of Washington, 1945. Vol. XXIII, 2d memoir.
3. Petrucci, et al. General Chemistry: Principles & Modern Applications. 9th ed. Upper Saddle River, New Jersey 2007.

Contributors and Attributions

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6.5: 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.

6.5.1: 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. How the pH changes during a titration is governed by the equilibrium reactions that surround the acid(s) and base(s) in the mixture.

The simplest acid-base reactions are those of a strong acid with a strong base. Table $6.5.1$ 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 $6.5.1$, 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 $6.5.1$ and Figure $6.5.1$).

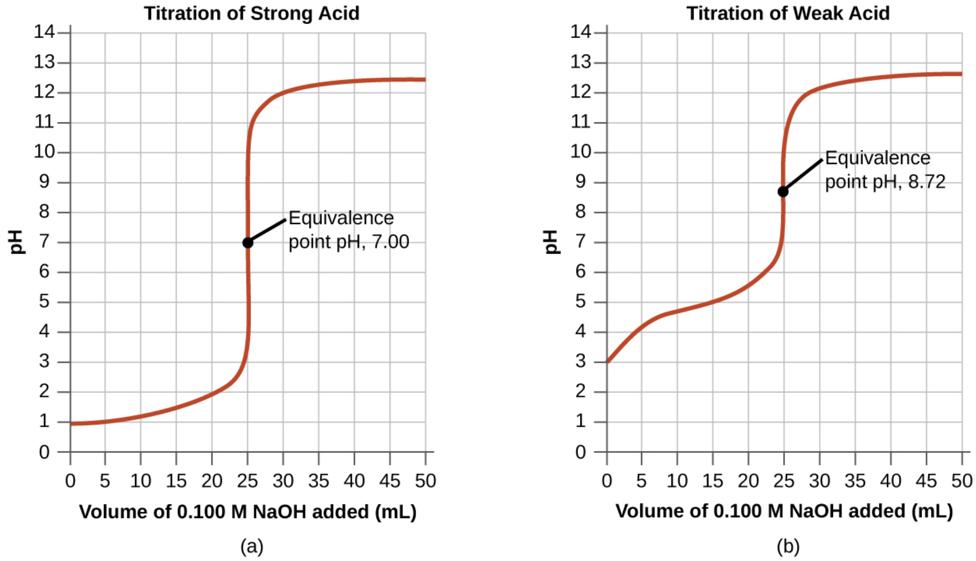

Figure $6.5.1$: (a) The titration curve for the titration of 25.00 mL of 0.100 M HCl (strong acid) with 0.100 M NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 M CH_3CO_2H (weak acid) with 0.100 M NaOH (strong base) has an equivalence point of 8.72 pH.

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 $6.5.1$ gives the pH values during the titration, Figure $6.5.1b$ 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:

$$\mathrm{CH_3CO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2H}(l) + \mathrm{OH^-}(aq) \tag{6.5.1}$$

After the equivalence point, the two curves are identical because the pH is dependent on the excess of hydroxide ion in both cases.

6.5.2: 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:

$$\underbrace{\mathrm{HIn(aq)}}_{\mathrm{red}} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \underbrace{\mathrm{In^-(aq)}}_{\mathrm{yellow}} \tag{6.5.2}$$

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{In^-}]}{[\mathrm{HIn}]} = 4.0 \times 10^{-4} \tag{6.5.3}$$

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:

$$\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]} = \frac{[\text{substance with yellow color}]}{[\text{substance with red color}]} = \frac{K_\mathrm{a}}{[\mathrm{H_3O^+}]} \tag{6.5.4}$$

Equation 6.5.4 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:

$$\frac{[H_3O^+]}{K_a} = \frac{[HIn]}{[In^-]} \tag{6.5.5}$$

$$\log\left(\frac{[H_3O^+]}{K_a}\right) = \log\left(\frac{[HIn]}{[In^-]}\right) \tag{6.5.6}$$

$$\log([H_3O^+]) - \log(K_a) = -\log\left(\frac{[In^-]}{[HIn]}\right) \tag{6.5.7}$$

$$-pH + pK_a = -\log\left(\frac{[In^-]}{[HIn]}\right) \tag{6.5.8}$$

$$pH = pK_a + \log\left(\frac{[In^-]}{[HIn]}\right) \tag{6.5.9}$$

or in general terms

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{6.5.10}$$

Equation 6.5.10 is the same as the *Henderson-Hasselbalch equation*, which can be used to describe the equilibrium of indicators.

When $[H_3O^+]$ has the same numerical value as K_a, the ratio of $[In^-]$ to [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 (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 6.5.2 presents several indicators, their colors, and their color-change intervals.

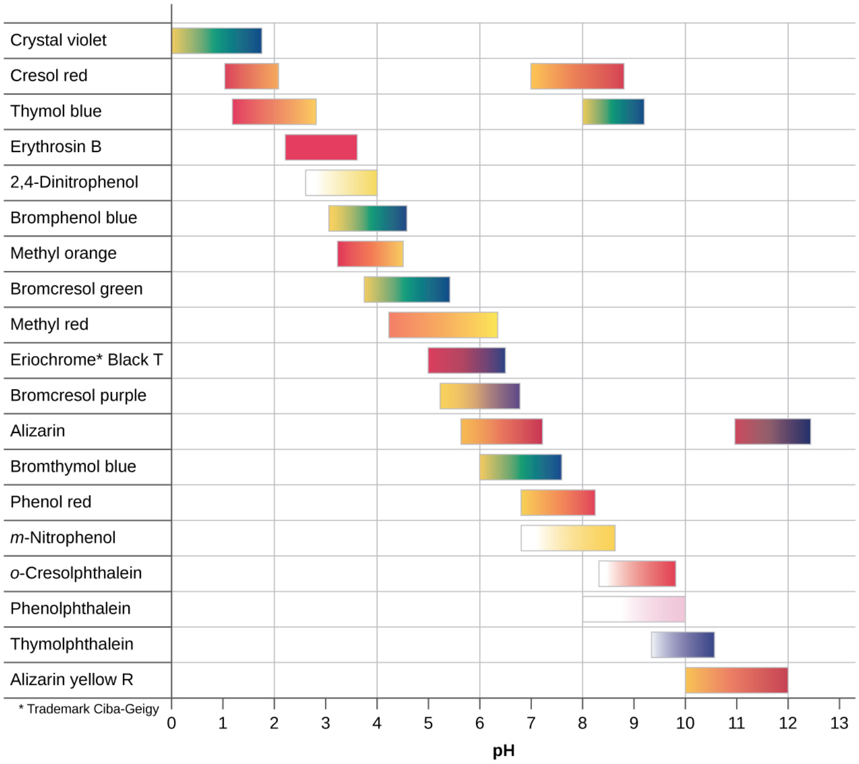

Figure 6.5.2: This chart illustrates the ranges of color change for several acid-base indicators.

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 6.5.3. 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.

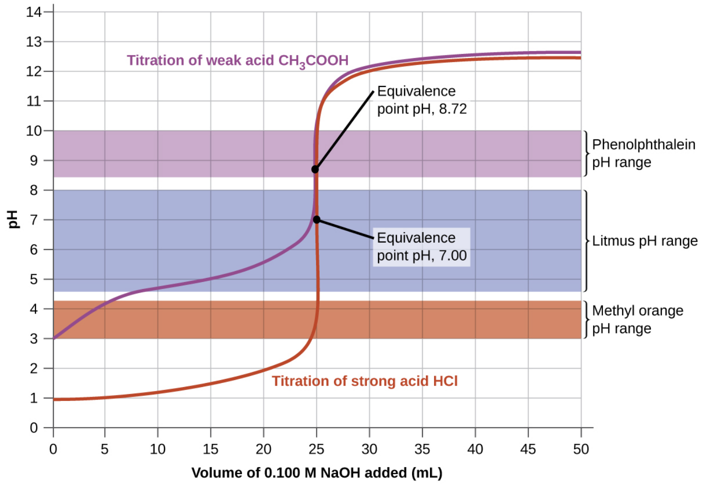

Figure 6.5.3: The graph shows a titration curve for the titration of 25.00 mL of 0.100 M CH_3CO_2H (weak acid) with 0.100 M NaOH (strong base) and the titration curve for the titration of HCl (strong acid) with NaOH (strong base). The pH ranges for the color change of phenolphthalein, litmus, and methyl orange are indicated by the shaded areas.

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 6.5.2 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 6.5.2 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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6.6: pH Calculations for Acid–Base Titrations

Acid–Base Titration Curves

In this section we will learn how to calculate the pH of an analyte solution throughout the titration, and use these values to prepare a titration curve. We also will learn how to sketch a good approximation of any acid–base titration curve using a limited number of simple calculations.

Titrating Strong Acids and Strong Bases

For our first titration curve, let's consider the titration of 50.0 mL of 0.100 M HCl using a titrant of 0.200 M NaOH. When a strong base and a strong acid react the only reaction of importance is

$$\mathrm{H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)} \tag{6.6.1}$$

The first task is to calculate the volume of NaOH needed to reach the equivalence point. At the equivalence point we know that

$$moles\ \mathrm{H_3O^+} = moles\ \mathrm{OH^-} \tag{6.6.2}$$

The volume of NaOH needed to reach the equivalence point is

$$50.0\ mL \times \frac{0.100\ mol\ HCl}{1000\ mL} \times \frac{1\ mol\ NaOH}{1\ mol\ HCl} \times \frac{1000\ mL\ NaOH}{0.200\ mol\ NaOH} = 25\ mL\ NaOH \tag{6.6.3}$$

Before the equivalence point, HCl is present in excess and the pH is determined by the concentration of unreacted HCl. At the start of the titration the solution is 0.100 M in HCl, which, because HCl is a strong acid, means the pH is

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log[\mathrm{HCl}] = -\log(0.100) = 1.00$$

After adding 10.0 mL of NaOH the concentration of excess HCl is

$$[\mathrm{HCl}] = \frac{(\mathrm{mol\ HCl})_{\mathrm{initial}} - (\mathrm{mol\ NaOH})_{\mathrm{added}}}{\mathrm{total\ volume}} = \frac{M_aV_a - M_bV_b}{V_a + V_b}$$

$$[\mathrm{HCl}] = \frac{(0.100\ \mathrm{M})(50.0\ \mathrm{mL}) - (0.200\ \mathrm{M})(10.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 10.0\ \mathrm{mL}} = 0.0500\ \mathrm{M}$$

and the pH increases to 1.30.

At the equivalence point the moles of HCl and the moles of NaOH are equal. Since neither the acid nor the base is in excess, the pH is determined by the dissociation of water.

$$K_w = 1.00 \times 10^{-14} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = [\mathrm{H_3O^+}]^2$$
$$[\mathrm{H_3O^+}] = 1.00 \times 10^{-7}$$

Thus, the pH at the equivalence point is 7.00.

For volumes of NaOH greater than the equivalence point, the pH is determined by the concentration of excess OH^-. For example, after adding 30.0 mL of titrant the concentration of OH^- is

$$[\mathrm{OH^-}] = \frac{(\mathrm{mol\ NaOH})_{\mathrm{added}} - (\mathrm{mol\ HCl})_{\mathrm{initial}}}{\mathrm{total\ volume}} = \frac{M_bV_b - M_aV_a}{V_a + V_b}$$

$$[\mathrm{OH^-}] = \frac{(0.200\ \mathrm{M})(30.0\ \mathrm{mL}) - (0.100\ \mathrm{M})(50.0\ \mathrm{mL})}{30.0\ \mathrm{mL} + 50.0\ \mathrm{mL}} = 0.0125\ \mathrm{M}$$

To find the concentration of H_3O^+ we use the K_w expression

$$[\mathrm{H_3O^+}] = \frac{K_\mathrm{w}}{[\mathrm{OH^-}]} = \frac{1.00 \times 10^{-14}}{0.0125} = 8.00 \times 10^{-13}\ \mathrm{M}$$

to find that the pH is 12.10. Table 6.6.1 and Figure 6.6.1 show additional results for this titration curve. You can use this same approach to calculate the titration curve for the titration of a strong base with a strong acid, except the strong base is in excess before the equivalence point and the strong acid is in excess after the equivalence point.

Table 6.6.1 . Titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH

volume of NaOH (mL)	pH	volume of NaOH (mL)	pH
0.00	1.00	26.0	11.42
5.00	1.14	28.0	11.89
10.0	1.30	30.0	12.10
15.0	1.51	35.0	12.37
20.0	1.85	40.0	12.52
22.0	2.08	45.0	12.63
24.0	2.57	50.0	12.70
25.0	7.00		

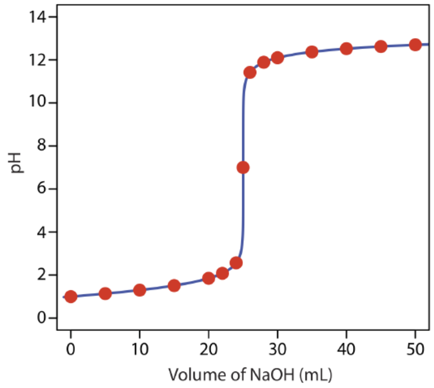


Figure 6.6.1 . Titration curve for the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH. The red points correspond to the data in Table 6.6.1 . The blue line shows the complete titration curve.

Exercise 6.6.1

Construct a titration curve for the titration of 25.0 mL of 0.125 M NaOH with 0.0625 M HCl.

Answer

The volume of HCl needed to reach the equivalence point is

$$V_{eq} = V_a = \frac{M_b V_b}{M_a} = \frac{(0.125 \text{ M})(25.0 \text{ mL})}{(0.0625 \text{ M})} = 50.0 \text{ mL}$$

Before the equivalence point, NaOH is present in excess and the pH is determined by the concentration of unreacted OH^-. For example, after adding 10.0 mL of HCl

$$\left[\text{OH}^-\right] = \frac{(0.125 \text{ M})(25.0 \text{ mL}) - (0.0625\text{M})(10.0 \text{ mL})}{25.0 \text{ mL} + 10.0 \text{ mL}} = 0.0714 \text{ M}$$

$$\left[\text{H}_3\text{O}^+\right] = \frac{K_w}{\left[\text{OH}^-\right]} = \frac{1.00 \times 10^{-14}}{0.0714 \text{ M}} = 1.40 \times 10^{-13} \text{ M}$$

the pH is 12.85.

For the titration of a strong base with a strong acid the pH at the equivalence point is 7.00.

For volumes of HCl greater than the equivalence point, the pH is determined by the concentration of excess HCl. For example, after adding 70.0 mL of titrant the concentration of HCl is

$$[\mathrm{HCl}] = \frac{(0.0625\ \mathrm{M})(70.0\ \mathrm{mL}) - (0.125\ \mathrm{M})(25.0\ \mathrm{mL})}{70.0\ \mathrm{mL} + 25.0\ \mathrm{mL}} = 0.0132\ \mathrm{M}$$

giving a pH of 1.88. Some additional results are shown here.

volume of HCl (mL)	pH	volume of HCl (mL)	pH
0	13.10	60	2.13
10	12.85	70	1.88
20	12.62	80	1.75
30	12.36	90	1.66
40	11.98	100	1.60
50	7.00		

Titrating a Weak Acid with a Strong Base

For this example, let’s consider the titration of 50.0 mL of 0.100 M acetic acid, CH_3COOH, with 0.200 M NaOH. Again, we start by calculating the volume of NaOH needed to reach the equivalence point; thus

$$\mathrm{mol\ \ CH_3COOH} = \mathrm{mol\ NaOH}$$

$$50.0\ mL\ \mathrm{CH_3COOH} \times \frac{0.100\ mol\ \mathrm{CH_3COOH}}{1000\ mL} \times \frac{1\ mol\ NaOH}{1\ mol} \times \frac{1000\ mL\ NaOH}{0.200\ mol\ NaOH} = 25.0\ mL\ NaOH \tag{6.6.4}$$

Before we begin the titration the pH is that for a solution of 0.100 M acetic acid. Because acetic acid is a weak acid, we calculate the pH using the acid equilibrium constant.

$$\mathrm{CH_3COOH}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3COO^-}(aq)$$

$$K_a = \frac{[\mathrm{H_3O^+}]\,[\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]} = \frac{(x)(x)}{0.100 - x} = 1.75 \times 10^{-5}$$

finding that the pH is 2.88.

Adding NaOH converts a portion of the acetic acid to its conjugate base, $CH_3COO^–$.

$$\mathrm{CH_3COOH}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{H_2O}(l) + \mathrm{CH_3COO^-}(aq) \tag{6.6.5}$$

> Because the equilibrium constant for reaction 6.6.5 is quite large
>
> $$K = K_\mathrm{a}/K_\mathrm{w} = 1.75 \times 10^9$$
>
> we can treat the reaction as if it goes to completion.

Any solution that contains comparable amounts of a weak acid, HA, and its conjugate weak base, $A^–$, is a buffer. We can calculate the pH of a buffer using the Henderson–Hasselbalch equation.

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

Before the equivalence point the concentration of unreacted acetic acid is

$$[\mathrm{CH_3COOH}] = \frac{(\mathrm{mol\ CH_3COOH})_\mathrm{initial} - (\mathrm{mol\ NaOH})_\mathrm{added}}{\mathrm{total\ volume}} = \frac{M_aV_a - M_bV_b}{V_a + V_b}$$

and the concentration of acetate is

$$[\mathrm{CH_3COO^-}] = \frac{(\text{mol NaOH})_{\text{added}}}{\text{total volume}} = \frac{M_b V_b}{V_a + V_b}$$

For example, after adding 10.0 mL of NaOH the concentrations of CH_3COOH and CH_3COO^- are

$$[\mathrm{CH_3COOH}] = \frac{(0.100\ \mathrm{M})(50.0\ \mathrm{mL}) - (0.200\ \mathrm{M})(10.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 10.0\ \mathrm{mL}} = 0.0500\ \mathrm{M}$$

$$\left[\mathrm{CH_3COO^-}\right] = \frac{(0.200\ \mathrm{M})(10.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 10.0\ \mathrm{mL}} = 0.0333\ \mathrm{M}$$

which gives us a pH of

$$\mathrm{pH} = 4.76 + \log \frac{0.0333\ \mathrm{M}}{0.0500\ \mathrm{M}} = 4.58$$

At the equivalence point the moles of acetic acid initially present and the moles of NaOH added are identical. Because their reaction effectively proceeds to completion, the predominate ion in solution is CH_3COO^-, which is a weak base. To calculate the pH we first determine the concentration of CH_3COO^-

$$\left[\mathrm{CH_3COO^-}\right] = \frac{(\text{mol NaOH})_{\text{added}}}{\text{total volume}} = \frac{(0.200\ \mathrm{M})(25.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 25.0\ \mathrm{mL}} = 0.0667\ \mathrm{M}$$

> Alternatively, we can calculate acetate’s concentration using the initial moles of acetic acid; thus
>
> $$\left[\mathrm{CH_3COO^-}\right] = \frac{(\text{mol CH}_3\text{COOH})_{\text{initial}}}{\text{total volume}} = \frac{(0.100\ \mathrm{M})(50.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 25.0\ \mathrm{mL}} = 0.0667\ \mathrm{M}$$

Next, we calculate the pH of the weak base.

$$\mathrm{CH_3COO^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OH^-}(aq) + \mathrm{CH_3COOH}(aq)$$

$$K_\mathrm{b} = \frac{\left[\mathrm{OH^-}\right][\mathrm{CH_3COOH}]}{\left[\mathrm{CH_3COO^-}\right]} = \frac{(x)(x)}{0.0667 - x} = 5.71 \times 10^{-10}$$

$$x = \left[\mathrm{OH^-}\right] = 6.17 \times 10^{-6}\ \mathrm{M}$$

$$\left[\mathrm{H_3O^+}\right] = \frac{K_\mathrm{w}}{\left[\mathrm{OH^-}\right]} = \frac{1.00 \times 10^{-14}}{6.17 \times 10^{-6}} = 1.62 \times 10^{-9}\ \mathrm{M}$$

finding that the pH at the equivalence point is 8.79.

After the equivalence point, the titrant is in excess and the titration mixture is a dilute solution of NaOH. We can calculate the pH using the same strategy as in the titration of a strong acid with a strong base. For example, after adding 30.0 mL of NaOH the concentration of OH^- is

$$\left[\mathrm{OH^-}\right] = \frac{(0.200\ \mathrm{M})(30.0\ \mathrm{mL}) - (0.100\ \mathrm{M})(50.0\ \mathrm{mL})}{30.0\ \mathrm{mL} + 50.0\ \mathrm{mL}} = 0.0125\ \mathrm{M}$$

$$\left[\mathrm{H_3O^+}\right] = \frac{K_\mathrm{w}}{\left[\mathrm{OH^-}\right]} = \frac{1.00 \times 10^{-14}}{0.0125} = 8.00 \times 10^{-13}\ \mathrm{M}$$

giving a pH of 12.10. Table 6.6.2 and Figure 6.6.2 show additional results for this titration. You can use this same approach to calculate the titration curve for the titration of a weak base with a strong acid, except the initial pH is determined by the weak base, the pH at the equivalence point by its conjugate weak acid, and the pH after the equivalence point by excess strong acid.

Table 6.6.2 . Titration of 50.0 mL of 0.100 M Acetic Acid with 0.200 M NaOH

volume of HCl (mL)	pH	volume of HCl (mL)	pH
0.00	2.88	26.0	11.43

5.00	4.16	28.0	11.89
10.0	4.58	30.0	12.10
15.0	4.94	35.0	12.37
20.0	5.36	40.0	12.52
22.0	5.63	45.0	12.63
24.0	6.14	50.0	12.70
25.0	8.79		

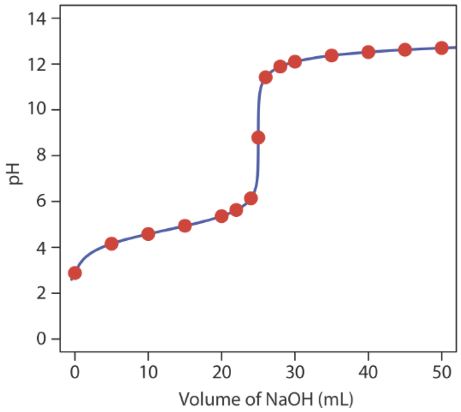


Figure 6.6.2 . Titration curve for the titration of 50.0 mL of 0.100 M CH_3COOH with 0.200 M NaOH. The red points correspond to the data in Table 6.6.2 . The blue line shows the complete titration curve.

Exercise 6.6.2

Construct a titration curve for the titration of 25.0 mL of 0.125 M NH_3 with 0.0625 M HCl.

Answer

The volume of HCl needed to reach the equivalence point is

$$V_{aq} = V_a = \frac{M_b V_b}{M_a} = \frac{(0.125\text{ M})(25.0\text{ mL})}{(0.0625\text{ M})} = 50.0\text{ mL}$$

Before adding HCl the pH is that for a solution of 0.100 M NH_3.

$$K_\text{b} = \frac{[\text{OH}^-]\left[\text{NH}_4^+\right]}{[\text{NH}_3]} = \frac{(x)(x)}{0.125 - x} = 1.75 \times 10^{-5}$$

$$x = \left[\text{OH}^-\right] = 1.48 \times 10^{-3}\text{ M}$$

$$\left[\text{H}_3\text{O}^+\right] = \frac{K_\text{w}}{\left[\text{OH}^-\right]} = \frac{1.00 \times 10^{-14}}{1.48 \times 10^{-3}\text{ M}} = 6.76 \times 10^{-12}\text{ M}$$

The pH at the beginning of the titration, therefore, is 11.17.

Before the equivalence point the pH is determined by an NH_3/NH_4^+ buffer. For example, after adding 10.0 mL of HCl

$$[\text{NH}_3] = \frac{(0.125\text{ M})(25.0\text{ mL}) - (0.0625\text{ M})(10.0\text{ mL})}{25.0\text{ mL} + 10.0\text{ mL}} = 0.0714\text{ M}$$

$$\left[\text{NH}_4^+\right] = \frac{(0.0625\text{ M})(10.0\text{ mL})}{25.0\text{ mL} + 10.0\text{ mL}} = 0.0179\text{ M}$$

$$\mathrm{pH}=9.244+\log \frac{0.0714 \mathrm{~M}}{0.0179 \mathrm{~M}}=9.84$$

At the equivalence point the predominate ion in solution is NH_4^+. To calculate the pH we first determine the concentration of NH_4^+

$$\left[\mathrm{NH}_4^{+}\right]=\frac{(0.125 \mathrm{~M})(25.0 \mathrm{~mL})}{25.0 \mathrm{~mL}+50.0 \mathrm{~mL}}=0.0417 \mathrm{~M}$$

and then calculate the pH

$$K_{\mathrm{a}}=\frac{\left[\mathrm{H}_3 \mathrm{O}^{+}\right]\left[\mathrm{NH}_3\right]}{\left[\mathrm{NH}_4^{+}\right]}=\frac{(x)(x)}{0.0417-x}=5.70 \times 10^{-10}$$

obtaining a value of 5.31.

After the equivalence point, the pH is determined by the excess HCl. For example, after adding 70.0 mL of HCl

$$[\mathrm{HCl}]=\frac{(0.0625 \mathrm{~M})(70.0 \mathrm{~mL})-(0.125 \mathrm{~M})(25.0 \mathrm{~mL})}{70.0 \mathrm{~mL}+25.0 \mathrm{~mL}}=0.0132 \mathrm{~M}$$

and the pH is 1.88. Some additional results are shown here.

volume of HCl (mL)	pH	volume of HCl (mL)	pH
0	11.17	60	2.13
10	9.84	70	1.88
20	9.42	80	1.75
30	9.07	90	1.66
40	8.64	100	1.60
50	5.31		

We can extend this approach for calculating a weak acid–strong base titration curve to reactions that involve multiprotic acids or bases, and mixtures of acids or bases. As the complexity of the titration increases, however, the necessary calculations become more time consuming. Not surprisingly, a variety of algebraic and spreadsheet approaches are available to aid in constructing titration curves.

The following papers provide information on algebraic approaches to calculating titration curves: (a) Willis, C. J. *J. Chem. Educ*. **1981**, *58*, 659–663; (b) Nakagawa, K. *J. Chem. Educ.* **1990**, *67*, 673–676; (c) Gordus, A. A. *J. Chem. Educ*. **1991**, *68*, 759–761; (d) de Levie, R. *J. Chem. Educ.* **1993**, *70*, 209–217; (e) Chaston, S. *J. Chem. Educ*. **1993**, *70*, 878–880; (f) de Levie, R. *Anal. Chem*. **1996**, *68*, 585–590.

The following papers provide information on the use of spreadsheets to generate titration curves: (a) Currie, J. O.; Whiteley, R. V. *J. Chem. Educ*. **1991**, *68*, 923–926; (b) Breneman, G. L.; Parker, O. J. *J. Chem. Educ*. **1992**, *69*, 46–47; (c) Carter, D. R.; Frye, M. S.; Mattson, W. A. *J. Chem. Educ*. **1993**, *70*, 67–71; (d) Freiser, H. *Concepts and Calculations in Analytical Chemistry*, CRC Press: Boca Raton, 1992.

Sketching an Acid–Base 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 an acid–base 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 CH_3COOH with 0.200 M NaOH to illustrate our approach. This is the same example that we used to develop the calculations for a weak acid–strong base titration curve. You can review the results of that calculation in Table 6.6.2 and in Figure 6.6.2 .

We begin by calculating the titration's equivalence point volume, which, as we determined earlier, is 25.0 mL. Next we draw our axes, placing pH on the *y*-axis and the titrant's volume on the *x*-axis. To indicate the equivalence point volume, we draw a vertical line that intersects the *x*-axis at 25.0 mL of NaOH. Figure 6.6.3 a shows the first step in our sketch.

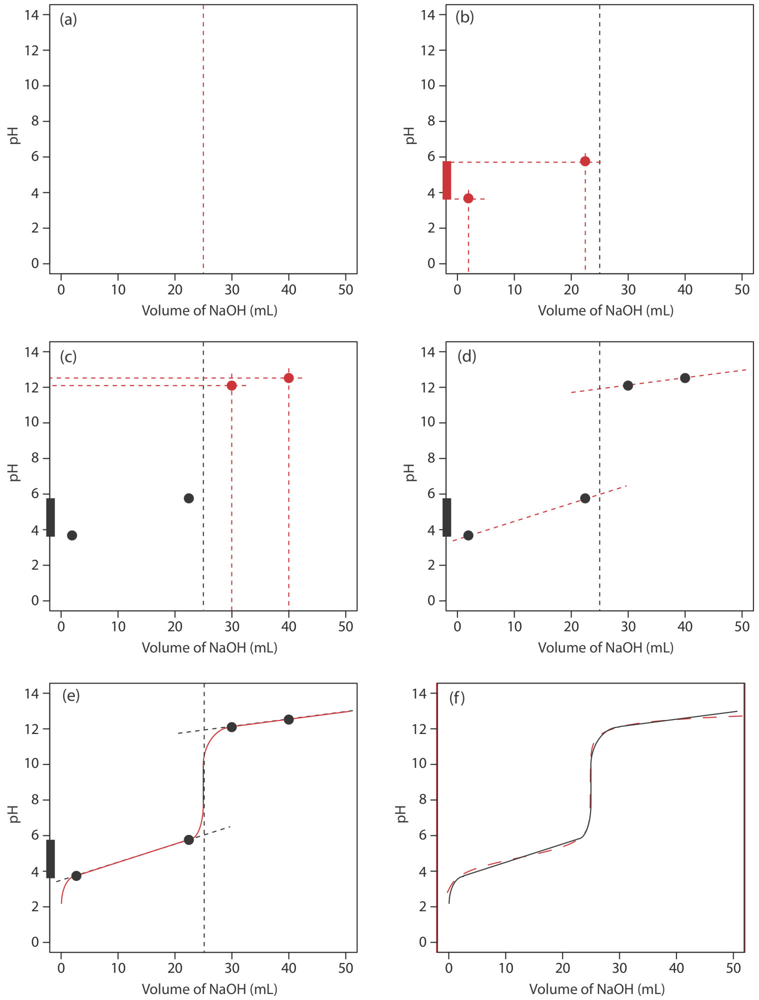


Figure 6.6.3 . Illustrations showing the steps used to sketch an approximate titration curve for the titration of 50.0 mL of 0.100 M CH_3COOH with 0.200 M NaOH: (a) locating the equivalence point volume; (b) plotting two points before the equivalence point; (c) plotting two points after the equivalence 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.

Before the equivalence point the titrand's pH is determined by a buffer of acetic acid, CH_3COOH, and acetate, CH_3COO^-. Although we can calculate a buffer's pH using the Henderson–Hasselbalch equation, we can avoid this calculation by making a simple assumption. You may recall from Chapter 6 that a buffer operates over a pH range that extends approximately ±1 pH unit on either side of the weak acid's pK_a value. The pH is at the lower end of this range, pH = pK_a – 1, when the weak acid's concentration is 10× greater than that of its conjugate weak base. The buffer reaches its upper pH limit, pH = pK_a + 1, when the weak acid's concentration is 10× smaller than that of its conjugate weak base. When we titrate a weak acid or a weak base, the buffer spans a range of volumes from approximately 10% of the equivalence point volume to approximately 90% of the equivalence point volume.

> The actual values are 9.09% and 90.9%, but for our purpose, using 10% and 90% is more convenient; that is, after all, one advantage of an approximation!

Figure 6.6.3 b shows the second step in our sketch. First, we superimpose acetic acid's ladder diagram on the *y*-axis, including its buffer range, using its pK_a value of 4.76. Next, we add two points, one for the pH at 10% of the equivalence point volume (a pH of

3.76 at 2.5 mL) and one for the pH at 90% of the equivalence point volume (a pH of 5.76 at 22.5 mL).

The third step is to add two points after the equivalence point. The pH after the equivalence point is fixed by the concentration of excess titrant, NaOH. Calculating the pH of a strong base is straightforward, as we saw earlier. Figure 6.6.3 c includes points (see Table 6.6.2) for the pH after adding 30.0 mL and after adding 40.0 mL of NaOH.

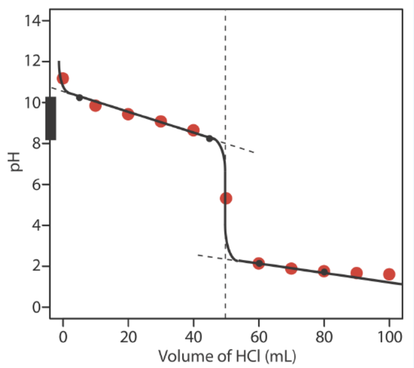
Next, we draw a straight line through each pair of points, extending each line through the vertical line that represents the equivalence point's volume (Figure 6.6.3 d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure 6.6.3 e). A comparison of our sketch to the exact titration curve (Figure 6.6.3 f) shows that they are in close agreement.

Exercise 6.6.3

Sketch a titration curve for the titration of 25.0 mL of 0.125 M NH_3 with 0.0625 M HCl and compare to the result from Exercise 6.6.2 .

Answer

The figure below shows a sketch of the titration curve. The black dots and curve are the approximate sketch of the titration curve. The points in red are the calculations from Exercise 6.6.2 . The two black points before the equivalence point (V_{HCl} = 5 mL, pH = 10.24 and V_{HCl} = 45 mL, pH= 8.24) are plotted using the pK_a of 9.244 for NH_4^+ . The two black points after the equivalence point (V_{HCl} = 60 mL, pH = 2.13 and V_{HCl} = 80 mL, pH= 1.75) are from the answer to Exercise 6.6.2 .



As shown in the following example, we can adapt this approach to any acid–base titration, including those where exact calculations are more challenging, including the titration of polyprotic weak acids and bases, and the titration of mixtures of weak acids or weak bases.

Example 6.6.1

Sketch titration curves for the following two systems: (a) the titration of 50.0 mL of 0.050 M H_2A, a diprotic weak acid with a pK_{a1} of 3 and a pK_{a2} of 7; and (b) the titration of a 50.0 mL mixture that contains 0.075 M HA, a weak acid with a pK_a of 3, and 0.025 M HB, a weak acid with a pK_a of 7. For both titrations, assume that the titrant is 0.10 M NaOH.

Solution

Figure 6.6.4 a shows the titration curve for H_2A, including the ladder diagram for H_2A on the *y*-axis, the two equivalence points at 25.0 mL and at 50.0 mL, two points before each equivalence point, two points after the last equivalence point, and the straight-lines used to sketch the final titration curve. Before the first equivalence point the pH is controlled by a buffer of H_2A and HA^-. An HA^-/A^{2-} buffer controls the pH between the two equivalence points. After the second equivalence point the pH reflects the concentration of excess NaOH.

Figure 6.6.4 b shows the titration curve for the mixture of HA and HB. Again, there are two equivalence points; however, in this case the equivalence points are not equally spaced because the concentration of HA is greater than that for HB. Because HA is the stronger of the two weak acids it reacts first; thus, the pH before the first equivalence point is controlled by a buffer of HA and A⁻. Between the two equivalence points the pH reflects the titration of HB and is determined by a buffer of HB and B⁻. After the second equivalence point excess NaOH determines the pH.

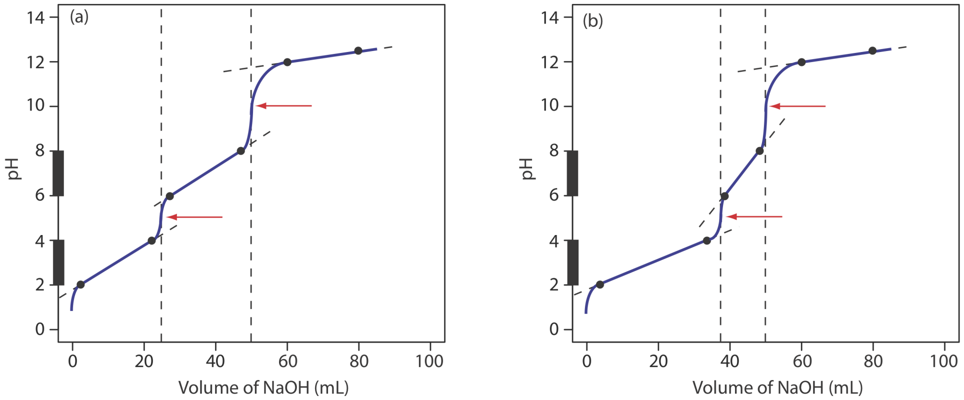


Figure 6.6.4 . Titration curves for Example 6.6.1 . The solid black dots show the points used to sketch the titration curves (shown in blue) and the red arrows show the locations of the equivalence points.

Exercise 6.6.4

Sketch the titration curve for 50.0 mL of 0.050 M H_2A, a diprotic weak acid with a pK_{a1} of 3 and a pK_{a2} of 4, using 0.100 M NaOH as the titrant. The fact that pK_{a2} falls within the buffer range of pK_{a1} presents a challenge that you will need to consider.

Answer

The figure below shows a sketch of the titration curve. The titration curve has two equivalence points, one at 25.0 mL $\left(\mathrm{H}_2\mathrm{A} \rightarrow \mathrm{HA}^-\right)$ and one at 50.0 mL $(\mathrm{HA}^- \rightarrow \mathrm{A}^{2-})$. In sketching the curve, we plot two points before the first equivalence point using the pK_{a1} of 3 for H_2A

$$V_{\mathrm{HCl}} = 2.5 \text{ mL}, \mathrm{pH} = 2 \text{ and } V_{\mathrm{HCl}} = 22.5 \text{ mL}, \mathrm{pH} = 4$$

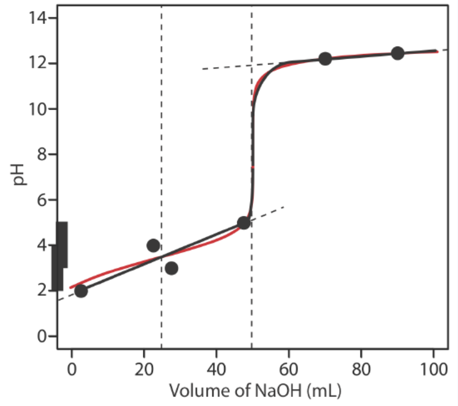
two points between the equivalence points using the pK_{a2} of 5 for HA^-

$$V_{\mathrm{HCl}} = 27.5 \text{ mL}, \mathrm{pH} = 3, \text{ and } V_{\mathrm{HCl}} = 47.5 \text{ mL}, \mathrm{pH} = 5$$

and two points after the second equivalence point

$$V_{\mathrm{HCl}} = 70 \text{ mL}, \mathrm{pH} = 12.22 \text{ and } V_{\mathrm{HCl}} = 90 \text{ mL}, \mathrm{pH} = 12.46$$

Drawing a smooth curve through these points presents us with the following dilemma—the pH appears to increase as the titrant's volume approaches the first equivalence point and then appears to decrease as it passes through the first equivalence point. This is, of course, absurd; as we add NaOH the pH cannot decrease. Instead, we model the titration curve before the second equivalence point by drawing a straight line from the first point (V_{HCl} = 2.5 mL, pH = 2) to the fourth point (V_{HCl} = 47.5 mL, pH= 5), ignoring the second and third points. The results is a reasonable approximation of the exact titration curve.



Selecting and Evaluating the End Point

Earlier we made an important distinction between a titration's end point and its equivalence point. The difference between these two terms is important and deserves repeating. An equivalence point, which occurs when we react stoichiometrically equal amounts of the analyte and the titrant, is a theoretical not an experimental value. A titration's end point is an experimental result that represents our best estimate of the equivalence point. Any difference between a titration's equivalence point and its corresponding end point is a source of determinate error.

Where is the Equivalence Point?

Earlier we learned how to calculate the pH at the equivalence point for the titration of a strong acid with a strong base, and for the titration of a weak acid with a strong base. We also learned how to sketch a titration curve with only a minimum of calculations. Can we also locate the equivalence point without performing any calculations. The answer, as you might guess, often is yes!

For most acid–base titrations the inflection point—the point on a titration curve that has the greatest slope—very nearly coincides with the titration's equivalence point. The red arrows in Figure 6.6.4 , for example, identify the equivalence points for the titration curves in Example 6.6.1 . An inflection point actually precedes its corresponding equivalence point by a small amount, with the error approaching 0.1% for weak acids and weak bases with dissociation constants smaller than $10^{–9}$, or for very dilute solutions [Meites, L.; Goldman, J. A. *Anal. Chim. Acta* **1963**, *29*, 472–479].

The principal limitation of an inflection point is that it must be present and easy to identify. For some titrations the inflection point is missing or difficult to find. Figure 6.6.5 , for example, demonstrates the affect of a weak acid's dissociation constant, K_a, on the shape of its titration curve. An inflection point is visible, even if barely so, for acid dissociation constants larger than $10^{–9}$, but is missing when K_a is $10^{–11}$.

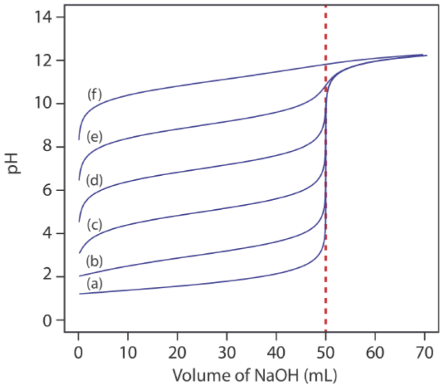


Figure 6.6.5 . Weak acid–strong base titration curves for the titration of 50.0 mL of 0.100 M HA with 0.100 M NaOH. The pK_a values for HA are (a) 1, (b) 3, (c) 5, (d) 7, (e) 9, and (f) 11. The dashed red line shows the equivalence point, which is 50.0 mL for all six analytes.

An inflection point also may be missing or difficult to see if the analyte is a multiprotic weak acid or weak base with successive dissociation constants that are similar in magnitude. To appreciate why this is true let's consider the titration of a diprotic weak acid, H_2A, with NaOH. During the titration the following two reactions occur.

$$H_2A(aq) + OH^-(aq) \longrightarrow H_2O(l) + HA^-(aq) \tag{6.6.6}$$

$$HA^-(aq) + OH^-(aq) \rightarrow H_2O(l) + A^{2-}(aq) \tag{6.6.7}$$

To see two distinct inflection points, reaction 6.6.6 must essentially be complete before reaction 6.6.7 begins.

Figure 6.6.6 shows titration curves for three diprotic weak acids. The titration curve for maleic acid, for which K_{a1} is approximately $20000\times$ larger than K_{a2}, has two distinct inflection points. Malonic acid, on the other hand, has acid dissociation constants that differ by a factor of approximately 690. Although malonic acid's titration curve shows two inflection points, the first is not as distinct as the second. Finally, the titration curve for succinic acid, for which the two K_a values differ by a factor of only $27\times$, has only a single inflection point that corresponds to the neutralization of $HC_2H_4O_4^-$ to $C_2H_4O_4^{2-}$. In general, we can detect separate inflection points when successive acid dissociation constants differ by a factor of at least 500 (a ΔK_a of at least 2.7).

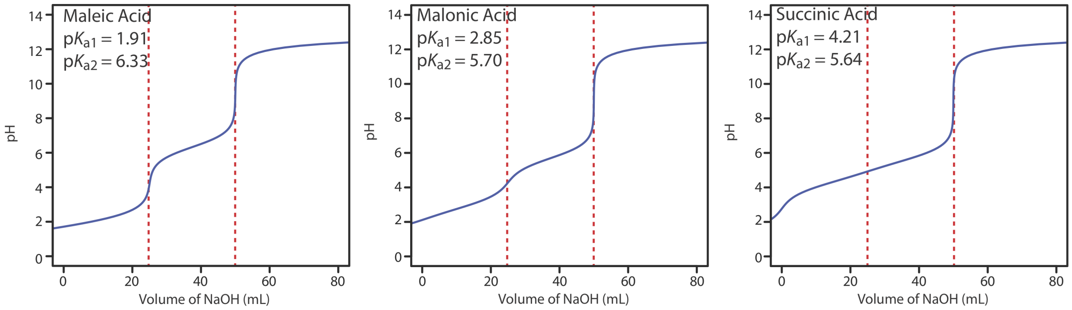


Figure 6.6.6 . Titration curves for the diprotic weak acids maleic acid, malonic acid, and succinic acid. Each titration curve is for 50.0 mL of 0.0500 M weak acid using 0.100 M NaOH as the titrant. Although each titration curve has equivalence points at 25.0 mL and 50.0 mL of NaOH (shown by the dashed red lines), the titration curve for succinic acid shows only one inflection point.

> The same holds true for mixtures of weak acids or mixtures of weak bases. To detect separate inflection points when titrating a mixture of weak acids, their pK_a values must differ by at least a factor of 500.

Finding the End Point with an Indicator

One interesting group of weak acids and weak bases are organic dyes. Because an organic dye has at least one highly colored conjugate acid–base species, its titration results in a change in both its pH and its color. We can use this change in color to indicate the end point of a titration provided that it occurs at or near the titration's equivalence point.

As an example, let's consider an indicator for which the acid form, HIn, is yellow and the base form, In^-, is red. The color of the indicator's solution depends on the relative concentrations of HIn and In^-. To understand the relationship between pH and color we use the indicator's acid dissociation reaction

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$

and its equilibrium constant expression.

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]} \tag{6.6.8}$$

Taking the negative log of each side of Equation 6.6.8, and rearranging to solve for pH leaves us with a equation that relates the solution's pH to the relative concentrations of HIn and In^-.

$$pH = pK_a + \log\frac{[In^-]}{[HIn]} \tag{6.6.9}$$

If we can detect HIn and In^- with equal ease, then the transition from yellow-to-red (or from red-to-yellow) reaches its midpoint, which is orange, when the concentrations of HIn and In^- are equal, or when the pH is equal to the indicator's pK_a. If the indicator's pK_a and the pH at the equivalence point are identical, then titrating until the indicator turns orange is a suitable end point. Unfortunately, we rarely know the exact pH at the equivalence point. In addition, determining when the concentrations of HIn and In^- are equal is difficult if the indicator's change in color is subtle.

We can establish the range of pHs over which the average analyst observes a change in the indicator's color by making two assumptions: that the indicator's color is yellow if the concentration of HIn is $10\times$ greater than that of In^- and that its color is red if the concentration of HIn is $10\times$ smaller than that of In^-. Substituting these inequalities into Equation 6.6.9

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{1}{10} = \mathrm{p}K_\mathrm{a} - 1$$

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{10}{1} = \mathrm{p}K_\mathrm{a} + 1$$

shows that the indicator changes color over a pH range that extends ±1 unit on either side of its $\mathrm{p}K_\mathrm{a}$. As shown in Figure 6.6.7 , the indicator is yel-ow when the pH is less than $\mathrm{p}K_\mathrm{a} - 1$ and it is red when the pH is greater than $\mathrm{p}K_\mathrm{a} + 1$. For pH values between $\mathrm{p}K_\mathrm{a} - 1$ and $\mathrm{p}K_\mathrm{a} + 1$ the indicator's color passes through various shades of orange. The properties of several common acid–base indicators are listed in Table 6.6.3 .

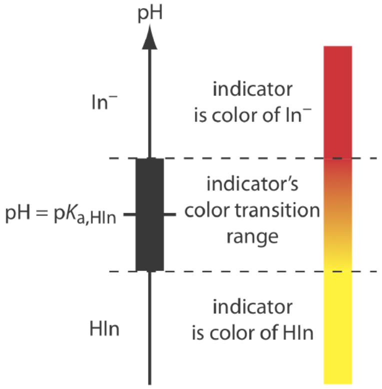


Figure 6.6.7 . Diagram showing the relationship between pH and an indicator's color. The ladder diagram defines pH values where HIn and In^- are the predominate species. The indicator changes color when the pH is between $\mathrm{p}K_\mathrm{a} - 1$ and $\mathrm{p}K_\mathrm{a}+1$.

Table 6.6.3 . Properties of Selected Acid–Base Indicators

indicator	acid color	base color	pH range	$\mathrm{p}K_\mathrm{a}$
cresol red	red	yellow	0.2–1.8	—
thymol blue	red	yellow	1.2–2.8	1.7
bromothymol blue	yellow	blue	3.0–4.6	4.1
methyl orange	red	yellow	3.4–4.4	3.7
Congo red	blue	red	3.0–5.0	—
bromocresol green	yellow	blue	3.8–5.4	4.7
methyl red	red	yellow	4.2–6.3	5.0
bromocresol purple	yellow	purple	5.2–6.8	6.1
litmus	red	blue	5.0–8.0	—
bromothymol blue	yellow	blue	6.0–7.6	7.1
phenol red	yellow	blue	6.8–8.4	7.8
cresol red	yellow	red	7.2–8.8	8.2
thymol blue	yellow	red	8.0–9.6	8.9
phenolphthalein	colorless	red	8.3–10.0	9.6
alizarin yellow R	yellow	orange-red	10.1–12.0	—

> You may wonder why an indicator's pH range, such as that for phenolphthalein, is not equally distributed around its $\mathrm{p}K_\mathrm{a}$ value. The explanation is simple. Figure 6.6.7 presents an idealized view in which our sensitivity to the indicator's two colors is

> equal. For some indicators only the weak acid or the weak base is colored. For other indicators both the weak acid and the weak base are colored, but one form is easier to see. In either case, the indicator's pH range is skewed in the direction of the indicator's less colored form. Thus, phenolphthalein's pH range is skewed in the direction of its colorless form, shifting the pH range to values lower than those suggested by Figure 6.6.7 .

The relatively broad range of pHs over which an indicator changes color places additional limitations on its ability to signal a titration's end point. To minimize a determinate titration error, the indicator's entire pH range must fall within the rapid change in pH near the equivalence point. For example, in Figure 6.6.8 we see that phenolphthalein is an appropriate indicator for the titration of 50.0 mL of 0.050 M acetic acid with 0.10 M NaOH. Bromothymol blue, on the other hand, is an inappropriate indicator because its change in color begins well before the initial sharp rise in pH, and, as a result, spans a relatively large range of volumes. The early change in color increases the probability of obtaining an inaccurate result, and the range of possible end point volumes increases the probability of obtaining imprecise results.

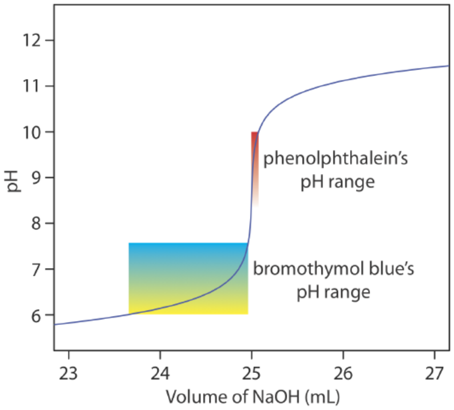


Figure 6.6.8 . Portion of the titration curve for 50.0 mL of 0.050 M CH_3COOH with 0.10 M NaOH, highlighting the region that contains the equivalence point. The end point transitions for the indicators phenolphthalein and bromothymol blue are superimposed on the titration curve.

? Exercise 6.6.5

Suggest a suitable indicator for the titration of 25.0 mL of 0.125 M NH_3 with 0.0625 M NaOH. You constructed a titration curve for this titration in Exercise 6.6.2 and Exercise 6.6.3 .

Answer

The pH at the equivalence point is 5.31 (see Exercise 6.6.2) and the sharp part of the titration curve extends from a pH of approximately 7 to a pH of approximately 4. Of the indicators in Table 6.6.3 , methyl red is the best choice because its pK_a value of 5.0 is closest to the equivalence point's pH and because the pH range of 4.2–6.3 for its change in color will not produce a significant titration error.

6.E: Acid-Base Equilibria (Exercises)

6.E.1: Polyprotic Acids

1. Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a 0.134-*M* solution of H_2CO_3, a diprotic acid:

- $[H_3O^+]$,
- $[OH^-]$
- $[H_2CO_3]$
- $[HCO_3^-]$
- $[CO_3^{2-}]$

No calculations are needed to answer this question.

Answer

$[H_3O^+]$ and $[HCO_3^-]$ are equal, H_3O^+ and HCO_3^- are practically equal

2. Calculate the concentration of each species present in a 0.050-*M* solution of H_2S.

3. Calculate the concentration of each species present in a 0.010-*M* solution of phthalic acid, $C_6H_4(CO_2H)_2$.

Answer

$$C_6H_4(CO_2H)_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2H)(CO_2)^-(aq) \qquad K_a = 1.1 \times 10^{-3}$$

$$C_6H_4(CO_2H)(CO_2)(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2)_2^{2-}(aq) \qquad K_a = 3.9 \times 10^{-6}$$

$[C_6H_4(CO_2H)_2]$ 7.2 × 10^{-3} *M*, $[C_6H_4(CO_2H)(CO_2)^-] = [H_3O^+]$ 2.8 × 10^{-3} *M*, $[C_6H_4(CO_2)_2^{2-}]$3.9 × 10^{-6} *M*, $[OH^-]$ 3.6 × 10^{-12} *M*

4. Salicylic acid, $HOC_6H_4CO_2H$, and its derivatives have been used as pain relievers for a long time. Salicylic acid occurs in small amounts in the leaves, bark, and roots of some vegetation (most notably historically in the bark of the willow tree). Extracts of these plants have been used as medications for centuries. The acid was first isolated in the laboratory in 1838.

a. Both functional groups of salicylic acid ionize in water, with $K_a = 1.0 \times 10^{-3}$ for the—CO_2H group and 4.2×10^{-13} for the −OH group. What is the pH of a saturated solution of the acid (solubility = 1.8 g/L)?

b. Aspirin was discovered as a result of efforts to produce a derivative of salicylic acid that would not be irritating to the stomach lining. Aspirin is acetylsalicylic acid, $CH_3CO_2C_6H_4CO_2H$. The $-CO_2H$ functional group is still present, but its acidity is reduced, $K_a = 3.0 \times 10^{-4}$. What is the pH of a solution of aspirin with the same concentration as a saturated solution of salicylic acid (See Part a)?

c. Under some conditions, aspirin reacts with water and forms a solution of salicylic acid and acetic acid:

$$CH_3CO_2C_6H_4CO_2H(aq) + H_2O(l) \longrightarrow HOC_6H_4CO_2H(aq) + CH_3CO_2H(aq) \tag{6.E.1}$$

d. Which of the acids salicylic acid or acetic acid produces more hydronium ions in solution such a solution?

e. What are the concentrations of molecules and ions in a solution produced by the hydrolysis of 0.50 g of aspirin dissolved in enough water to give 75 mL of solution?

5. The ion HTe^- is an amphiprotic species; it can act as either an acid or a base.

a. Wh at is K_a for the acid reaction of HTe^- with H_2O?
b. What is K_b for the reaction in which HTe^- functions as a base in water?
c. Demonstrate whether or not the second ionization of H_2Te can be neglected in the calculation of $[HTe^-]$ in a 0.10 M solution of H_2Te.

Answer

a. (K_{\ce a2}=1×10^{−5};\)
b. $K_b = 4.3 \times 10^{-12}$;

c. $\frac{[\mathrm{Te}^{2-}][\mathrm{H_3O^+}]}{[\mathrm{HTe}^-]} = \frac{(x)(0.0141+x)}{(0.0141-x)} \approx \frac{(x)(0.0141)}{0.0141} = 1\times10^{-5}$. Solving for x gives 1×10^{-5} M. Therefore, compared with 0.014 M, this value is negligible (0.071%).

6.E.2: Buffers

6. Explain why a buffer can be prepared from a mixture of NH_4Cl and NaOH but not from NH_3 and NaOH.

7. Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid H_3PO_4 and a salt of its conjugate base NaH_2PO_4.

Answer

Excess H_3O^+ is removed primarily by the reaction:

$\mathrm{H_3O^+}(aq) + \mathrm{H_2PO_4^-}(aq) \longrightarrow \mathrm{H_3PO_4}(aq) + \mathrm{H_2O}(l)$ Excess base is removed by the reaction: $\mathrm{OH^-}(aq) + \mathrm{H_3PO_4}(aq) \longrightarrow \mathrm{H_2PO_4^-}(aq) + \mathrm{H_2O}(l)$

8. Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base NH_3 and a salt of its conjugate acid NH_4Cl.

9. What is $[H_3O^+]$ in a solution of 0.25 M CH_3CO_2H and 0.030 M $NaCH_3CO_2$?

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \qquad K_\mathrm{a} = 1.8\times10^{-5}$$

Answer

$[H_3O^+] = 1.5 \times 10^{-4}$ M

10. What is $[H_3O^+]$ in a solution of 0.075 M HNO_2 and 0.030 M $NaNO_2$?

Answer

$$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{NO_2^-}(aq) \qquad K_\mathrm{a} = 4.5\times10^{-5}$$

11. What is $[OH^-]$ in a solution of 0.125 M CH_3NH_2 and 0.130 M CH_3NH_3Cl?

Answer

$$\mathrm{CH_3NH_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3NH_3^+}(aq) + \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 4.4\times10^{-4}$$

$[OH^-] = 4.2 \times 10^{-4}$ M

12. What is $[OH^-]$ in a solution of 1.25 M NH_3 and 0.78 M NH_4NO_3?

Answer

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 1.8\times10^{-5}$$

13. What concentration of NH_4NO_3 is required to make $[OH^-] = 1.0 \times 10^{-5}$ in a 0.200-M solution of NH_3?

Answer

$[NH_4NO_3] = 0.36$ M

14. What concentration of NaF is required to make $[H_3O^+] = 2.3 \times 10^{-4}$ in a 0.300-M solution of HF?

15. What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:

a. HCl
b. KCH_3CO_2
c. NaCl
d. KOH
e. CH_3CO_2H

Answer

a. The added HCl will increase the concentration of H_3O^+ slightly, which will react with $CH_3CO_2^-$ and produce CH_3CO_2H in the process. Thus, $[CH_3CO_2^-]$ decreases and $[CH_3CO_2H]$ increases.

b. The added KCH_3CO_2 will increase the concentration of $[CH_3CO_2^-]$ which will react with H_3O^+ and produce CH_3CO_2 H in the process. Thus, $[H_3O^+]$ decreases slightly and $[CH_3CO_2H]$ increases.

c. The added NaCl will have no effect on the concentration of the ions.

d. The added KOH will produce OH^- ions, which will react with the H_3O^+, thus reducing $[H_3O^+]$. Some additional CH_3CO_2H will dissociate, producing $[CH_3CO_2^-]$ ions in the process. Thus, $[CH_3CO_2H]$ decreases slightly and $[CH_3CO_2^-]$ increases.

e. The added CH_3CO_2H will increase its concentration, causing more of it to dissociate and producing more $[CH_3CO_2^-]$ and H_3O^+ in the process. Thus, $[H_3O^+]$ increases slightly and $[CH_3CO_2^-]$ increases.

16. What is the effect on the concentration of ammonia, hydroxide ion, and ammonium ion when the following are added to a basic buffer solution of equal concentrations of ammonia and ammonium nitrate:

a. KI
b. NH_3
c. HI
d. NaOH
e. NH_4Cl

17. What will be the pH of a buffer solution prepared from 0.20 mol NH_3, 0.40 mol NH_4NO_3, and just enough water to give 1.00 L of solution?

Answer

pH = 8.95

18. Calculate the pH of a buffer solution prepared from 0.155 mol of phosphoric acid, 0.250 mole of KH_2PO_4, and enough water to make 0.500 L of solution.

19. How much solid $NaCH_3CO_2•3H_2O$ must be added to 0.300 L of a 0.50-*M* acetic acid solution to give a buffer with a pH of 5.00? (Hint: Assume a negligible change in volume as the solid is added.)

Answer

37 g (0.27 mol)

20. What mass of NH_4Cl must be added to 0.750 L of a 0.100-*M* solution of NH_3 to give a buffer solution with a pH of 9.26? (Hint: Assume a negligible change in volume as the solid is added.)

21. A buffer solution is prepared from equal volumes of 0.200 *M* acetic acid and 0.600 *M* sodium acetate. Use 1.80×10^{-5} as K_a for acetic acid.

a. What is the pH of the solution?

b. Is the solution acidic or basic?

22. What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to 0.200 L of the original buffer?

a. pH = 5.222;
b. The solution is acidic. (c) pH = 5.221

23. A 5.36–g sample of NH_4Cl was added to 25.0 mL of 1.00 *M* NaOH and the resulting solution diluted to 0.100 L.

a. What is the pH of this buffer solution?
b. Is the solution acidic or basic?
c. What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to the solution?

24. Which acid in [link] is most appropriate for preparation of a buffer solution with a pH of 3.1? Explain your choice.

Answer

To prepare the best buffer for a weak acid HA and its salt, the ratio $\frac{[H_3O^+]}{K_a}$ should be as close to 1 as possible for effective buffer action. The [H_3O^+] concentration in a buffer of pH 3.1 is [H_3O^+] = $10^{-3.1}$ = 7.94 × 10^{-4} *M*

We can now solve for K_a of the best acid as follows:

$$\frac{[H_3O^+]}{K_a} = 1$$

$$K_a = \frac{[H_3O^+]}{1} = 7.94 \times 10^{-4}$$

In [link], the acid with the closest K_a to 7.94 × 10^{-4} is HF, with a K_a of 7.2 × 10^{-4}.

25. Which acid in [link] is most appropriate for preparation of a buffer solution with a pH of 3.7? Explain your choice.

26. Which base in [link] is most appropriate for preparation of a buffer solution with a pH of 10.65? Explain your choice.

Answer

For buffers with pHs > 7, you should use a weak base and its salt. The most effective buffer will have a ratio $\frac{[OH^-]}{K_b}$ that is as close to 1 as possible. The pOH of the buffer is 14.00 − 10.65 = 3.35. Therefore, [OH^-] is [OH^-] = 10^{-pOH} = $10^{-3.35}$ = 4.467 × 10^{-4} *M*.

We can now solve for K_b of the best base as follows: $\frac{[OH^-]}{K_b} = 1$ K_b = [OH^-] = 4.47 × 10^{-4} In [link], the base with the closest K_b to 4.47 × 10^{-4} is CH_3NH_2, with a K_b = 4.4 × 10^{-4}.

27. Which base in [link] is most appropriate for preparation of a buffer solution with a pH of 9.20? Explain your choice.

28. Saccharin, $C_7H_4NSO_3H$, is a weak acid (K_a = 2.1 × 10^{-2}). If 0.250 L of diet cola with a buffered pH of 5.48 was prepared from 2.00 × 10^{-3} g of sodium saccharide, Na($C_7H_4NSO_3$), what are the final concentrations of saccharine and sodium saccharide in the solution?

Answer

The molar mass of sodium saccharide is 205.169 g/mol. Using the abbreviations HA for saccharin and NaA for sodium saccharide the number of moles of NaA in the solution is:

9.75 × 10^{-6} mol. This ionizes initially to form saccharin ions, A^-, with: [A^-] = 3.9 × 10^{-5} *M*

29. What is the pH of 1.000 L of a solution of 100.0 g of glutamic acid ($C_5H_9NO_4$, a diprotic acid; K_1 = 8.5 × 10^{-5}, K_2 = 3.39 × 10^{-10}) to which has been added 20.0 g of NaOH during the preparation of monosodium glutamate, the flavoring agent? What is the pH when exactly 1 mol of NaOH per mole of acid has been added?

6.E.3: Acid-Base Titrations

30. Explain how to choose the appropriate acid-base indicator for the titration of a weak base with a strong acid.

Answer

At the equivalence point in the titration of a weak base with a strong acid, the resulting solution is slightly acidic due to the presence of the conjugate acid. Thus, pick an indicator that changes color in the acidic range and brackets the pH at the equivalence point. Methyl orange is a good example.

31. Explain why an acid-base indicator changes color over a range of pH values rather than at a specific pH.

32. Why can we ignore the contribution of water to the concentrations of H_3O^+ in the solutions of following acids:

- 0.0092 *M* HClO, a weak acid
- 0.0810 *M* HCN, a weak acid
- 0.120 *M* $Fe(H_2O)_6^{2+}$ a weak acid, K_a = 1.6 × 10^{-7}

but not the contribution of water to the concentration of OH^-?

Answer

In an acid solution, the only source of OH^- ions is water. We use K_w to calculate the concentration. If the contribution from water was neglected, the concentration of OH^- would be zero.

33. Why can we ignore the contribution of water to the concentration of OH^- in a solution of the following bases:

$0.0784\ M\ C_6H_5NH_2$, a weak base

$0.11\ M\ (CH_3)_3N$, a weak base

but not the contribution of water to the concentration of H_3O^+?

34. Draw a curve for a series of solutions of HF. Plot $[H_3O^+]_{total}$ on the vertical axis and the total concentration of HF (the sum of the concentrations of both the ionized and nonionized HF molecules) on the horizontal axis. Let the total concentration of HF vary from $1 \times 10^{-10}\ M$ to $1 \times 10^{-2}\ M$.

Answer

A graph is shown that is titled "Plot of [H subscript 3 O superscript +] Against [H F]." The horizontal axis is labeled "[H F], M." The axis begins at 10 superscript negative 10 and includes markings every 10 superscript 2 units up to 1.0. The vertical axis is labeled "[H subscript 3 O superscript plus], M" and begins at 10 superscript negative 10 and increases by 10 superscript 2 up to 1.0. A black curve starts at the left side of the graph at (10 superscript negative 10, 10 superscript negative 7). The line extends horizontally to a horizontal axis value of 10 superscript negative 8. After this, the line gradually increases at a steady rate to a value just over 10 superscript negative 3 at a horizontal axis value of 10 superscript negative 2.

35. Draw a curve similar to that shown in Figure for a series of solutions of NH_3. Plot $[OH^-]$ on the vertical axis and the total concentration of NH_3 (both ionized and nonionized NH_3 molecules) on the horizontal axis. Let the total concentration of NH_3 vary from $1 \times 10^{-10}\ M$ to $1 \times 10^{-2}\ M$.

36. Calculate the pH at the following points in a titration of 40 mL (0.040 L) of 0.100 *M* barbituric acid ($K_a = 9.8 \times 10^{-5}$) with 0.100 *M* KOH.

a. no KOH added

b. 20 mL of KOH solution added

c. 39 mL of KOH solution added

d. 40 mL of KOH solution added

e. 41 mL of KOH solution added

Answer

a. pH = 2.50; b. pH = 4.01; c. pH = 5.60; d. pH = 8.35; e. pH = 11.08

37. The indicator dinitrophenol is an acid with a K_a of 1.1×10^{-4}. In a 1.0×10^{-4}-*M* solution, it is colorless in acid and yellow in base. Calculate the pH range over which it goes from 10% ionized (colorless) to 90% ionized (yellow).

CHAPTER OVERVIEW

7: Solubility and Complex-Ion Equilibria

7.1: Solubility Product Constant, Ksp

Learning Objectives

- Define the solubility product, K_{sp}, for a sparingly soluble compound
- To calculate the solubility of an ionic compound from its K_{sp}

The focus of this chapter is the equilibrium of ions in solution. When a sparingly soluble ionic compound is added to water, the amount of the compound that dissolves is defined by the equilibrium constant for the system. 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:

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)} \tag{7.1.1}$$

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

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 \tag{7.1.2}$$

At 25°C and pH 7.00, K_{sp} 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 7.1.1, which shows that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH, changes in pH can affect the solubility of a compound as discussed later.

Table 7.1.1: Solubility Products for Selected Ionic Substances at 25°C

Solid	Color	K_{sp}	Solid	Color	K_{sp}
Acetates			**Iodides**		
$Ca(O_2CCH_3)_2 \cdot 3H_2O$	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			$MgC_2O_4 \cdot 2H_2O$	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**		
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}

*These contain the $Hg_2{}^{2+}$ ion.

Solid	Color	K_{sp}		Solid	Color	K_{sp}
$PbCrO_4$	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.

Definition of a Solubility Product: https://youtu.be/VzxSmH_iwHE

Example 7.1.1

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}.

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:

$$\mathrm{Ca(O_2CCO_2)\cdot H_2O(s) \rightleftharpoons Ca^{2+}(aq) + {}^-O_2CCO_2^-(aq) + H_2O(l)} \quad K_{\mathrm{sp}} = [\mathrm{Ca^{2+}}][\mathrm{ox^{2-}}]$$

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:

$$\frac{7.36 \times 10^{-4}\ \mathrm{g}}{146.1\ \mathrm{g/mol}} = 5.04 \times 10^{-6}\ \mathrm{mol\ Ca(O_2CCO_2)\cdot H_2O}$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$\left(\frac{5.04 \times 10^{-6}\ \mathrm{mol\ Ca(O_2CCO_2\cdot)H_2O}}{100\ \mathrm{mL}}\right)\left(\frac{1000\ \mathrm{mL}}{1.00\ \mathrm{L}}\right) = 5.04 \times 10^{-5}\ \mathrm{mol/L} = 5.04 \times 10^{-5}\ \mathrm{M}$$

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,

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (5.04 \times 10^{-5})(5.04 \times 10^{-5}) = 2.54 \times 10^{-9} \tag{7.1.3}$$

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 7.1.1

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}

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 7.1.1. 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 7.1.2

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 ???) 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.

$$\mathbf{Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)}$$

	$Ca_3(PO_4)_2$	$[Ca^{2+}]$	$[PO_4^{3-}]$
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):

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3x)^3(2x)^2 \tag{7.1.4}$$

$$2.07 \times 10^{-33} = 108x^5 \tag{7.1.5}$$

$$1.92 \times 10^{-35} = x^5 \tag{7.1.6}$$

$$1.14 \times 10^{-7}\text{ M} = x \tag{7.1.7}$$

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:

$$\left(\frac{1.14 \times 10^{-7}\text{ mol}}{1\text{ L}}\right) 100\text{ mL} \left(\frac{1\text{ L}}{1000\text{ mL}}\right) \left(\frac{310.18\text{ g } Ca_3(PO_4)_2}{1\text{ mol}}\right) = 3.54 \times 10^{-6}\text{ g } Ca_3(PO_4)_2$$

? Exercise 7.1.2

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
b. 3.54 mg

The Ion Product

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.

As summarized in Figure 7.1.1 "The Relationship between ", 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.

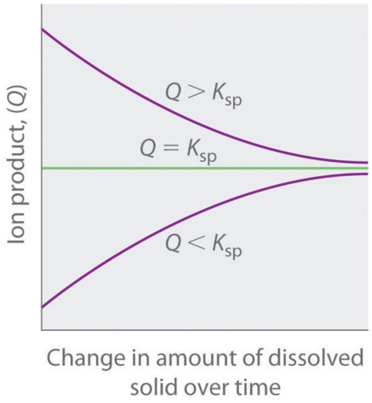


Figure 7.1.1: The Relationship between Q and K_{sp}. If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium ($Q = K_{sp}$). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until $Q = K_{sp}$. If $Q = K_{sp}$, 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.

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 7.1.3

We mentioned that 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 $BaSO_4$ because NaCl is highly soluble. The equation for the precipitation of $BaSO_4$ is as follows:

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)} \tag{7.1.8}$$

The solubility product expression is as follows:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.08{\times}10^{-10}$$

B To solve this problem, we must first calculate the ion product—$Q = [Ba^{2+}][SO_4^{2-}]$—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 $BaCl_2$ 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):

$$\text{moles } SO_4^{2-} = 10.0\text{ mL}\left(\frac{1\text{ L}}{1000\text{ mL}}\right)\left(\frac{0.0020\text{ mol}}{1\text{ L}}\right) = 2.0\times 10^{-5}\text{ mol } SO_4^{2-}$$

$$[SO_4^{2-}] = \left(\frac{2.0\times 10^{-5}\text{ mol } SO_4^{2-}}{110\text{ mL}}\right)\left(\frac{1000\text{ mL}}{1\text{ L}}\right) = 1.8\times 10^{-4}\text{ M } SO_4^{2-}$$

We can now calculate Q:

$$Q = [Ba^{2+}][SO_4^{2-}] = (2.9\times10^{-4})(1.8\times10^{-4}) = 5.2\times10^{-8}$$

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 $[Ba^{2+}][SO_4^{2-}] = K_{sp} = 1.08 \times 10^{-10}$.

? Exercise 7.1.3

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 2.0×10^{-5}M solution of $Ca(NO_3)_2$, will CaF_2 precipitate?

Answer yes ($Q = 4.7 \times 10^{-11} > K_{sp}$)

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. In contrast, the ion product (Q) 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.

7.2: Relationship Between Solubility and Ksp

Learning Objectives

- Quantitatively related K_{sp} to solubility

Considering the relation between solubility and K_{sp} is important when describing the solubility of slightly ionic compounds. However, this article discusses ionic compounds that are difficult to dissolve; they are considered "slightly soluble" or "almost insoluble." Solubility product constants (K_{sq}) are given to those solutes, and these constants can be used to find the molar solubility of the compounds that make the solute. This relationship also facilitates finding the K_{sq} of a slightly soluble solute from its solubility.

Introduction

Recall that the definition of *solubility* is the maximum possible concentration of a solute in a solution at a given temperature and pressure. We can determine the solubility product of a slightly soluble solid from that measure of its solubility at a given temperature and pressure, provided that the only significant reaction that occurs when the solid dissolves is its dissociation into solvated ions, that is, the only equilibrium involved is:

$$\mathrm{M}_p\mathrm{X}_q(s) \rightleftharpoons p\mathrm{M}^{\mathrm{m}+}(aq) + q\mathrm{X}^{\mathrm{n}-}(aq) \tag{7.2.1}$$

In this case, we calculate the solubility product by taking the solid's solubility expressed in units of moles per liter (mol/L), known as its **molar solubility**.

Calculation of K_{sp} from Equilibrium Concentrations

We began the chapter with an informal discussion of how the mineral fluorite is formed. Fluorite, $\mathrm{CaF_2}$, is a slightly soluble solid that dissolves according to the equation:

$$\mathrm{CaF_2}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + 2\,\mathrm{F^-}(aq)$$

The concentration of $\mathrm{Ca^{2+}}$ in a saturated solution of $\mathrm{CaF_2}$ is 2.1 × 10^{-4} *M*; therefore, that of $\mathrm{F^-}$ is 4.2 × 10^{-4} *M*, that is, twice the concentration of $\mathrm{Ca^{2\,+}}$. What is the solubility product of fluorite?

Solution

First, write out the K_{sp} expression, then substitute in concentrations and solve for K_{sp}:

$$\mathrm{CaF_2(s)} \rightleftharpoons \mathrm{Ca^{2\,+}(aq)} + 2\,\mathrm{F^-(aq)}$$

A saturated solution is a solution at equilibrium with the solid. Thus:

$$\begin{aligned} K_{\mathrm{sp}} &= [\mathrm{Ca^{2\,+}}][\mathrm{F^-}]^2 \\ &= (2.1 \times 10^{-4})(4.2 \times 10^{-4})^2 \\ &= 3.7 \times 10^{-11} \end{aligned}$$

As with other equilibrium constants, we do not include units with K_{sp}.

Exercise 7.2.1

In a saturated solution that is in contact with solid $\mathrm{Mg(OH)_2}$, the concentration of $\mathrm{Mg^{2+}}$ is 3.7 × 10^{-5} *M*. What is the solubility product for $\mathrm{Mg(OH)_2}$?

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq)$$

Answer

2.0 × 10^{-13}

Determination of Molar Solubility from K_{sp}

The K_{sp} of copper(I) bromide, $CuBr$, is 6.3 × 10^{-9}. Calculate the molar solubility of copper bromide.

Solution

The solubility product constant of copper(I) bromide is 6.3 × 10^{-9}.

The reaction is:

$$\mathrm{CuBr}(s) \rightleftharpoons \mathrm{Cu}^+(aq) + \mathrm{Br}^-(aq)$$

First, write out the solubility product equilibrium constant expression:

$$K_{\mathrm{sp}} = [\mathrm{Cu}^+][\mathrm{Br}^-]$$

Create an ICE table (as introduced in the chapter on fundamental equilibrium concepts), leaving the $CuBr$ column empty as it is a solid and does not contribute to the K_{sp}:

	$CuBr$ $\rightleftharpoons$	**Cu^+ +**	**Br^-**
Initial concentration (*M*)		0	0
Change (*M*)		*x*	*x*
Equilibrium concentration (*M*)		0 + *x* = *x*	0 + *x* = *x*

At equilibrium:

$$\begin{aligned} K_{\mathrm{sp}} &= [\mathrm{Cu}^+][\mathrm{Br}^-] \\ 6.3 \times 10^{-9} &= (x)(x) = x^2 \\ x &= \sqrt{(6.3 \times 10^{-9})} = 7.9 \times 10^{-5} \end{aligned}$$

Therefore, the molar solubility of $CuBr$ is 7.9 × 10^{-5} *M*.

Finding the Solubility of a Salt: https://youtu.be/98BuldrICXM

Summary

Solubility is defined as the maximum amount of solute that can be dissolved in a solvent at equilibrium. Equilibrium is the state at which the concentrations of products and reactant are constant after the reaction has taken place. The solubility product constant (K_{sp}) describes the equilibrium between a solid and its constituent ions in a solution. The value of the constant identifies the degree to which the compound can dissociate in water. The higher the K_{sp}, the more soluble the compound is. K_{sq} is defined in terms of activity rather than concentration because it is a measure of a concentration that depends on certain conditions such as temperature, pressure, and composition. It is influenced by surroundings. K_{sp} is used to describe the saturated solution of ionic compounds. (A saturated solution is in a state of equilibrium between the dissolved, dissociated, undissolved solid, and the ionic compound.)

Contributors and Attributions

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7.3: Common-Ion Effect in Solubility Equilibria

Learning Objectives

- Recognize common ions from various salts, acids, and bases.
- Calculate concentrations involving common ions.
- Calculate ion concentrations involving chemical equilibrium.

The common-ion effect is used to describe the effect on an equilibrium involving a substance that adds an ion that is a part of the equilibrium.

Introduction

The solubility products K_{sp}'s are equilibrium constants in hetergeneous equilibria (i.e., between two different phases). If several salts are present in a system, they all ionize in the solution. If the salts contain a common cation or anion, these salts contribute to the concentration of the common ion. Contributions from all salts must be included in the calculation of concentration of the common ion. For example, a solution containing sodium chloride and potassium chloride will have the following relationship:

$$[\mathrm{Na^+}] + [\mathrm{K^+}] = [\mathrm{Cl^-}] \tag{7.3.1}$$

Consideration of *charge balance* or *mass balance* or both leads to the same conclusion. The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant. Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions. Adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion. The exceptions generally involve the formation of complex ions, which is discussed later.

Common Ions

When NaCl and KCl are dissolved in the same solution, the $\mathrm{Cl^-}$ ions are *common* to both salts. In a system containing NaCl and KCl, the $\mathrm{Cl^-}$ ions are common ions.

$$\begin{gathered}
\mathrm{NaCl} \rightleftharpoons \mathrm{Na^+} + \mathrm{Cl^-} \\
\mathrm{KCl} \rightleftharpoons \mathrm{K^+} + \mathrm{Cl^-} \\
\mathrm{CaCl_2} \rightleftharpoons \mathrm{Ca^{2+}} + 2\mathrm{Cl^-} \\
\mathrm{AlCl_3} \rightleftharpoons \mathrm{Al^{3+}} + 3\mathrm{Cl^-} \\
\mathrm{AgCl} \rightleftharpoons \mathrm{Ag^+} + \mathrm{Cl^-}
\end{gathered}$$

For example, when AgCl is dissolved into a solution already containing NaCl (actually $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions), the $\mathrm{Cl^-}$ ions come from the ionization of both AgCl and NaCl. Thus, $[\mathrm{Cl^-}]$ differs from $[\mathrm{Ag^+}]$. The following examples show how the concentration of the common ion is calculated.

Example 7.3.1

What are $[\mathrm{Na^+}]$, $[\mathrm{Cl^-}]$, $[\mathrm{Ca^{2+}}]$, and $[\mathrm{H^+}]$ in a solution containing 0.10 M each of NaCl, $\mathrm{CaCl_2}$, and HCl?

Solution

Due to the conservation of ions, we have

$$[\mathrm{Na^+}] = [\mathrm{Ca^{2+}}] = [\mathrm{H^+}] = 0.10\ \mathrm{M}.$$

but

$$\begin{aligned}
[\mathrm{Cl^-}] = {} & 0.10\ (\text{due to }\mathrm{NaCl}) \\
& + 0.20\ (\text{due to }\mathrm{CaCl_2}) \\
& + 0.10\ (\text{due to }\mathrm{HCl}) \\
= {} & 0.40\ \mathrm{M}
\end{aligned} \tag{7.3.2}$$

Exercise 7.3.1

John poured 10.0 mL of 0.10 M NaCl, 10.0 mL of 0.10 M KOH, and 5.0 mL of 0.20 M HCl solutions together and then he made the total volume to be 100.0 mL. What is $[\mathrm{Cl}^-]$ in the final solution?

$$[\mathrm{Cl}^-] = \frac{0.1\ \mathrm{M} \times 10\ \mathrm{mL} + 0.2\ \mathrm{M} \times 5.0\ \mathrm{mL}}{100.0\ \mathrm{mL}} = 0.020\ \mathrm{M}$$

Le Châtelier's Principle states that if an equilibrium becomes unbalanced, the reaction will shift to restore the balance. If a common ion is added to a weak acid or weak base equilibrium, then the equilibrium will shift towards the reactants, in this case the weak acid or base.

Example 7.3.2

Consider the lead(II) ion concentration in this *saturated* solution of $PbCl_2$. The balanced reaction is

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

Defining s as the concentration of dissolved lead(II) chloride, then:

$$[Pb^{2+}] = s$$

$$[Cl^-] = 2s$$

These values can be substituted into the solubility product expression, which can be solved for s:

$$\begin{aligned} K_{sp} &= [Pb^{2+}][Cl^-]^2 \\ &= s \times (2s)^2 \\ 1.7 \times 10^{-5} &= 4s^3 \\ s^3 &= \frac{1.7 \times 10^{-5}}{4} \\ &= 4.25 \times 10^{-6} \\ s &= \sqrt[3]{4.25 \times 10^{-6}} \\ &= 1.62 \times 10^{-2}\ mol\ dm^{-3} \end{aligned}$$

The concentration of lead(II) ions in the solution is 1.62 x 10^{-2} M. Consider what happens if sodium chloride is added to this saturated solution. Sodium chloride shares an ion with lead(II) chloride. The chloride ion is **common** to both of them; this is the origin of the term "common ion effect".

Look at the original equilibrium expression again:

$$PbCl_2\ (s) \rightleftharpoons Pb^{2+}\ (aq) + 2Cl^-\ (aq)$$

What happens to that equilibrium if extra chloride ions are added? According to *Le* Châtelier, the position of equilibrium will shift to counter the change, in this case, by removing the chloride ions by making extra solid lead(II) chloride.

Of course, the concentration of lead(II) ions in the solution is so small that only a tiny proportion of the extra chloride ions can be converted into solid lead(II) chloride. The lead(II) chloride becomes even *less soluble*, and the concentration of lead(II) ions in the solution *decreases*. This type of response occurs with any sparingly soluble substance: it is less soluble in a solution which contains any ion which it has in common. This is the common ion effect.

A Simple Example

If an attempt is made to dissolve some lead(II) chloride in some 0.100 M sodium chloride solution instead of in water, what is the equilibrium concentration of the lead(II) ions this time? As before, define s to be the concentration of the lead(II) ions.

$$[Pb^{2+}] = s \tag{7.3.3}$$

The calculations are different from before. This time the concentration of the chloride ions is governed by the concentration of the sodium chloride solution. The number of ions coming from the lead(II) chloride is going to be tiny compared with the 0.100 M coming from the sodium chloride solution. In calculations like this, it can be assumed that the concentration of the common ion is entirely due to the other solution. This simplifies the calculation.

So we assume:

$$[Cl^-] = 0.100\ M \tag{7.3.4}$$

The rest of the mathematics looks like this:

$$\begin{aligned} K_{sp} &= [Pb^{2+}][Cl^-]^2 \\ &= s \times (0.100)^2 \\ 1.7 \times 10^{-5} &= s \times 0.00100 \end{aligned} \tag{7.3.5}$$

therefore:

$$\begin{aligned} s &= \frac{1.7 \times 10^{-5}}{0.0100} \\ &= 1.7 \times 10^{-3} \text{ M} \end{aligned} \tag{7.3.6}$$

Finally, compare that value with the simple saturated solution:

Original solution:

$$[Pb^{2+}] = 0.0162\ M \tag{7.3.7}$$

Solution in 0.100 M NaCl solution:

$$[Pb^{2+}] = 0.0017\ M \tag{7.3.8}$$

The concentration of the lead(II) ions has decreased by a factor of about 10. If more concentrated solutions of sodium chloride are used, the solubility decreases further.

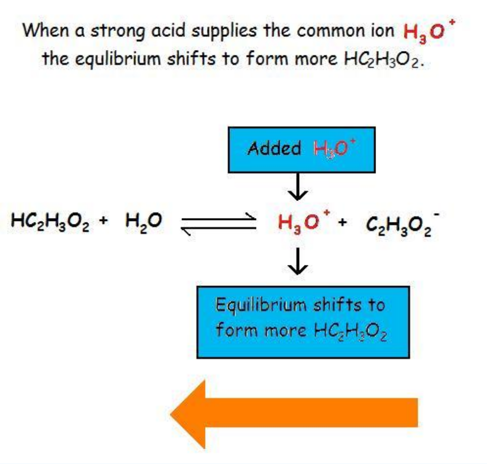
> Adding a common ion to a system at equilibrium affects the equilibrium composition, but **not** the ionization constant.

Common Ion Effect with Weak Acids and Bases

Adding a common ion prevents the weak acid or weak base from ionizing as much as it would without the added common ion. The common ion effect suppresses the ionization of a weak acid by adding more of an ion that is a product of this equilibrium.

✓ Example 7.3.3

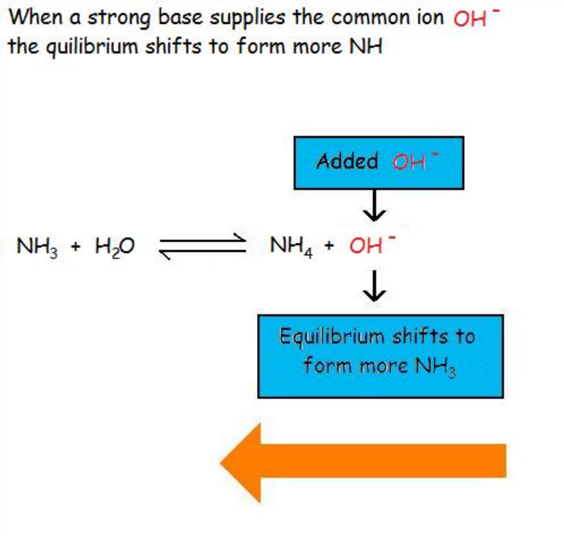
The common ion effect of H_3O^+ on the ionization of acetic acid



The common ion effect suppresses the ionization of a weak base by adding more of an ion that is a product of this equilibrium.

Example 7.3.4

Consider the common ion effect of OH⁻ on the ionization of ammonia



Adding the common ion of hydroxide shifts the reaction towards the left to decrease the stress (in accordance with Le Châtelier's Principle), forming more reactants. This decreases the reaction quotient, because the reaction is being pushed towards the left to reach equilibrium. The equilibrium constant, $K_b = 1.8 \times 10^{-5}$, does not change. The reaction is put out of balance, or equilibrium.

$$Q_a = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

At first, when more hydroxide is added, the quotient is greater than the equilibrium constant. The reaction then shifts right, causing the denominator to increase, decreasing the reaction quotient and pulling towards equilibrium and causing Q to decrease towards K.

Common Ion Effect on Solubility

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$].

$$\mathrm{Ca_3(PO_4)_2(s) \rightleftharpoons 3\,Ca^{2+}(aq) + 2\,PO_4^{3-}(aq)} \tag{7.3.9}$$

We have seen that the solubility of $Ca_3(PO_4)_2$ in water at 25°C is 1.14×10^{-7} M ($K_{sp} = 2.07 \times 10^{-33}$). Thus a saturated solution of $Ca_3(PO_4)_2$ in water contains

$$3 \times (1.14 \times 10^{-7}\ M) = 3.42 \times 10^{-7}\ M\,\mathrm{Ca^{2+}} \tag{7.3.10}$$

and

$$2 \times (1.14 \times 10^{-7}\ M) = 2.28 \times 10^{-7}\ M\,\mathrm{PO_4^{3-}} \tag{7.3.11}$$

according to the stoichiometry shown in Equation 7.3.9 (neglecting hydrolysis to form HPO_4^{2-}). If $CaCl_2$ is added to a saturated solution of $Ca_3(PO_4)_2$, the Ca^{2+} ion concentration will increase such that $[Ca^{2+}] > 3.42 \times 10^{-7}$ M, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 7.3.9 to proceed to the left, resulting in precipitation of $\mathrm{Ca_3(PO_4)_2}$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{sp}$.

> *Adding a common ion decreases solubility, as the reaction shifts toward the left to relieve the stress of the excess product. Adding a common ion to a dissociation reaction causes*

> *the equilibrium to shift left, toward the reactants, causing precipitation.*

Example 7.3.5

Consider the reaction:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

What happens to the solubility of $PbCl_2(s)$ when 0.1 M NaCl is added?

Solution

$$K_{sp} = 1.7 \times 10^{-5}$$

$$Q_{sp} = 1.8 \times 10^{-5}$$

Identify the common ion: Cl^-

Notice: $Q_{sp} > K_{sp}$ The addition of NaCl has caused the reaction to shift out of equilibrium because there are more dissociated ions. Typically, solving for the molarities requires the assumption that the solubility of $PbCl_2$ is equivalent to the concentration of Pb^{2+} produced because they are in a 1:1 ratio.

Because K_{sp} for the reaction is 1.7×10^{-5}, the overall reaction would be $(s)(2s)^2= 1.7\times10^{-5}$. Solving the equation for s gives $s= 1.62\times10^{-2}$ M. The coefficient on Cl^- is 2, so it is assumed that twice as much Cl^- is produced as Pb^{2+}, hence the '2s.' The solubility equilibrium constant can be used to solve for the molarities of the ions at equilibrium.

The molarity of Cl^- added would be 0.1 M because Na^+ and Cl^- are in a 1:1 ration in the ionic salt, NaCl. Therefore, the overall molarity of Cl^- would be 2s + 0.1, with 2s referring to the contribution of the chloride ion from the dissociation of lead chloride.

$$\begin{aligned} Q_{sp} &= [Pb^{2+}][Cl^-]^2 \\ 1.8\times10^{-5} &= (s)(2s+0.1)^2 \qquad (7.3.12) \\ s &= [Pb^{2+}] \\ &= 1.8\times10^{-3} M \\ 2s &= [Cl^-] \\ &\approx 0.1 M \qquad (7.3.13) \end{aligned}$$

Notice that the molarity of Pb^{2+} is lower when NaCl is added. The equilibrium constant remains the same because of the increased concentration of the chloride ion. To simplify the reaction, it can be assumed that $[Cl^-]$ is approximately 0.1M since the formation of the chloride ion from the dissociation of lead chloride is so small. The reaction quotient for $PbCl_2$ is greater than the equilibrium constant because of the added Cl^-. This therefore shift the reaction left towards equilibrium, causing precipitation and lowering the current solubility of the reaction. Overall, the solubility of the reaction decreases with the added sodium chloride.

> The common ion effect usually decreases the solubility of a sparingly soluble salt.

Example 7.3.6

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.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)} \tag{7.3.14}$$

	$Ca_3(PO_4)_2$	**$[Ca^{2+}]$**	**$[PO_4{}^{3-}]$**
initial	pure solid	0.20	0
change	—	$+3x$	$+2x$
final	pure solid	$0.20 + 3x$	$2x$

B The K_{sp} expression is as follows:

$$K_{sp} = [Ca^{2+}]^3[PO_4{}^{3-}]^2 = (0.20 + 3x)^3(2x)^2 = 2.07\times10^{-33}$$

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:

$$\begin{aligned} K_{\text{sp}} = (0.20)^3(2x)^2 &= 2.07 \times 10^{-33} \\ x^2 &= 6.5 \times 10^{-32} \\ x &= 2.5 \times 10^{-16} \text{ M} \end{aligned}$$

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 7.3.2—here the initial $[Ca^{2+}]$ was 0.20 M rather than 0.

? Exercise 7.3.4

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)

The Common Ion Effect in Solubility Products: https://youtu.be/_P3wozLs0Tc

Summary

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.

Contributors and Attributions

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7.4: Criteria for Precipitation and its Completeness

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

$$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{CO_3^{2-}}(aq) \tag{7.4.1}$$

We can establish this equilibrium either by adding solid calcium carbonate to water or by mixing a solution that contains calcium ions with a solution that contains carbonate ions. If we add calcium carbonate to water, the solid will dissolve until the concentrations are such that the value of the reaction quotient $(\mathrm{Q{=}[Ca^{2+}][CO_3^{2-}]})$ is equal to the solubility product (K_{sp} = 4.8 × 10^{-9}). If we mix a solution of calcium nitrate, which contains Ca^{2+} ions, with a solution of sodium carbonate, which contains $\mathrm{CO_3^{2-}}$ ions, the slightly soluble ionic solid $CaCO_3$ will precipitate, provided that the concentrations of Ca^{2+} and $\mathrm{CO_3^{2-}}$ ions are such that Q is greater than K_{sp} for the mixture. The reaction shifts to the left and the concentrations of the ions are reduced by formation of the solid until the value of Q equals K_{sp}. A saturated solution in equilibrium with the undissolved solid will result. If the concentrations are such that Q is less than K_{sp}, then the solution is not saturated and no precipitate will form.

We can compare numerical values of Q with K_{sp} to predict whether precipitation will occur, as Example 7.4.7 shows. (Note: Since all forms of equilibrium constants are temperature dependent, we will assume a room temperature environment going forward in this chapter unless a different temperature value is explicitly specified.)

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of lime, $Ca(OH)_2$, a readily available inexpensive source of OH^- ion:

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \quad K_{\mathrm{sp}} = 2.1\times10^{-13} \tag{7.4.2}$$

The concentration of $Mg^{2+}(aq)$ in sea water is 0.0537 M. Will $Mg(OH)_2$ precipitate when enough $Ca(OH)_2$ is added to give a $[OH^-]$ of 0.0010 M?

Solution

This problem asks whether the reaction:

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \tag{7.4.3}$$

shifts to the left and forms solid $Mg(OH)_2$ when $[Mg^{2+}]$ = 0.0537 M and $[OH^-]$ = 0.0010 M. The reaction shifts to the left if Q is greater than K_{sp}. Calculation of the reaction quotient under these conditions is shown here:

$$\mathrm{Q} = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2 = (0.0537)(0.0010)^2 = 5.4\times10^{-8} \tag{7.4.4}$$

Because Q is greater than K_{sp} (Q = 5.4 × 10^{-8} is larger than K_{sp} = 2.1 × 10^{-13}), we can expect the reaction to shift to the left and form solid magnesium hydroxide. $Mg(OH)_2(s)$ forms until the concentrations of magnesium ion and hydroxide ion are reduced sufficiently so that the value of Q is equal to K_{sp}.

? Exercise 7.4.1

Use the solubility products in Appendix J to determine whether $CaHPO_4$ will precipitate from a solution with $[Ca^{2+}]$ = 0.0001 M and $[\mathrm{HPO_4^{2-}}]$ = 0.001 M.

Answer

No precipitation of $CaHPO_4$; Q = 1 × 10^{-7}, which is less than K_{sp}

✓ Precipitation of AgCl upon Mixing Solutions

Does silver chloride precipitate when equal volumes of a 2.0 × 10^{-4}-M solution of $AgNO_3$ and a 2.0 × 10^{-4}-M solution of NaCl are mixed?

(Note: The solution also contains Na^+ and $\mathrm{NO_3^-}$ ions, but when referring to solubility rules, one can see that sodium nitrate is very soluble and cannot form a precipitate.)

Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{Cl}^{-}(aq)$$

The solubility product is 1.8×10^{-10} (see Appendix J).

AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of $AgNO_3$ and NaCl is greater than K_{sp}. The volume doubles when we mix equal volumes of $AgNO_3$ and NaCl solutions, so each concentration is reduced to half its initial value. Consequently, immediately upon mixing, $[Ag^+]$ and $[Cl^-]$ are both equal to:

$$\frac{1}{2}(2.0 \times 10^{-4})\ M = 1.0 \times 10^{-4}\ M$$

The reaction quotient, Q, is *momentarily* greater than K_{sp} for AgCl, so a supersaturated solution is formed:

$$Q = [\mathrm{Ag}^{+}][\mathrm{Cl}^{-}] = (1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8} > K_{sp}$$

Since supersaturated solutions are unstable, AgCl will precipitate from the mixture until the solution returns to equilibrium, with Q equal to K_{sp}.

? Exercise 7.4.2

Will $KClO_4$ precipitate when 20 mL of a 0.050-M solution of K^+ is added to 80 mL of a 0.50-M solution of ClO_4^-? (Remember to calculate the new concentration of each ion after mixing the solutions before plugging into the reaction quotient expression.)

Answer

No, $Q = 4.0 \times 10^{-3}$, which is less than $K_{sp} = 1.07 \times 10^{-2}$

In the previous two examples, we have seen that $Mg(OH)_2$ or AgCl precipitate when Q is greater than K_{sp}. In general, when a solution of a soluble salt of the M^{m+} ion is mixed with a solution of a soluble salt of the X^{n-} ion, the solid, M_pX_q precipitates if the value of Q for the mixture of M^{m+} and X^{n-} is greater than K_{sp} for M_pX_q. Thus, if we know the concentration of one of the ions of a slightly soluble ionic solid and the value for the solubility product of the solid, then we can calculate the concentration that the other ion must exceed for precipitation to begin. To simplify the calculation, we will assume that precipitation begins when the reaction quotient becomes equal to the solubility product constant.

✓ Precipitation of Calcium Oxalate

Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion, $C_2O_4^{2-}$, for this purpose (Figure 7.4.4). At sufficiently high concentrations, the calcium and oxalate ions form solid, $CaC_2O_4 \cdot H_2O$ (which also contains water bound in the solid). The concentration of Ca^{2+} in a sample of blood serum is 2.2×10^{-3} M. What concentration of $C_2O_4^{2-}$ ion must be established before $CaC_2O_4 \cdot H_2O$ begins to precipitate?

Figure 7.4.4: Anticoagulants can be added to blood that will combine with the Ca^{2+} ions in blood serum and prevent the blood from clotting. (credit: modification of work by Neeta Lind)

Solution

The equilibrium expression is:

$$\mathrm{CaC_2O_4}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{C_2O_4^{2-}}(aq) \tag{7.4.5}$$

For this reaction:

$$K_\mathrm{sp} = [\mathrm{Ca^{2+}}][\mathrm{C_2O_4^{2-}}] = 2.27 \times 10^{-9} \tag{7.4.6}$$

(see Appendix J)

CaC_2O_4 does not appear in this expression because it is a solid. Water does not appear because it is the solvent.

Solid CaC_2O_4 does not begin to form until Q equals K_{sp}. Because we know K_{sp} and $[Ca^{2+}]$, we can solve for the concentration of $C_2O_4^{2-}$ that is necessary to produce the first trace of solid:

$$\begin{aligned} Q = K_\mathrm{sp} = [\mathrm{Ca^{2+}}][\mathrm{C_2O_4^{2-}}] &= 2.27 \times 10^{-9} \\ (2.2 \times 10^{-3})[\mathrm{C_2O_4^{2-}}] &= 2.27 \times 10^{-9} \\ [\mathrm{C_2O_4^{2-}}] = \frac{2.27 \times 10^{-9}}{2.2 \times 10^{-3}} &= 1.0 \times 10^{-6} \end{aligned}$$

A concentration of $[C_2O_4^{2-}] = 1.0 \times 10^{-6}\ M$ is necessary to initiate the precipitation of CaC_2O_4 under these conditions.

Exercise 7.4.3

If a solution contains 0.0020 mol of CrO_4^{2-} per liter, what concentration of Ag^+ ion must be reached by adding solid $AgNO_3$ before Ag_2CrO_4 begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

Answer:

$7.0 \times 10^{-5}\ M$

It is sometimes useful to know the concentration of an ion that remains in solution after precipitation. We can use the solubility product for this calculation too: If we know the value of K_{sp} and the concentration of one ion in solution, we can calculate the concentration of the second ion remaining in solution. The calculation is of the same type as that in Example—calculation of the concentration of a species in an equilibrium mixture from the concentrations of the other species and the equilibrium constant. However, the concentrations are different; we are calculating concentrations after precipitation is complete, rather than at the start of precipitation.

✓ Concentrations Following Precipitation

Clothing washed in water that has a manganese $[Mn^{2+}(aq)]$ concentration exceeding 0.1 mg/L ($1.8 \times 10^{-6}\ M$) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be reduced by adding a base. If a person doing laundry wishes to add a buffer to keep the pH high enough to precipitate the manganese as the hydroxide, $Mn(OH)_2$, what pH is required to keep $[Mn^{2+}]$ equal to $1.8 \times 10^{-6}\ M$?

Solution The dissolution of $Mn(OH)_2$ is described by the equation:

$$\mathrm{Mn(OH)_2}(s) \rightleftharpoons \mathrm{Mn^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \quad K_\mathrm{sp} = 4.5 \times 10^{-14} \tag{7.4.7}$$

We need to calculate the concentration of OH^- when the concentration of Mn^{2+} is $1.8 \times 10^{-6}\ M$. From that, we calculate the pH. At equilibrium:

$$K_\mathrm{sp} = [\mathrm{Mn^{2+}}][\mathrm{OH^-}]^2 \tag{7.4.8}$$

or

$$(1.8 \times 10^{-6})[\mathrm{OH^-}]^2 = 4.5 \times 10^{-14} \tag{7.4.9}$$

so

$$[\mathrm{OH^-}] = 1.6 \times 10^{-4}\ M \tag{7.4.10}$$

Now we calculate the pH from the pOH:

$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.6 \times 10^{-4}) = 3.80$$
$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.80 = 10.20$$

If the person doing laundry adds a base, such as the sodium silicate (Na_4SiO_4) in some detergents, to the wash water until the pH is raised to 10.20, the manganese ion will be reduced to a concentration of 1.8×10^{-6} *M*; at that concentration or less, the ion will not stain clothing.

Exercise 7.4.4

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of $Ca(OH)_2$. The concentration of $Mg^{2+}(aq)$ in sea water is 5.37×10^{-2} *M*. Calculate the pH at which $[Mg^{2+}]$ is diminished to 1.0×10^{-5} *M* by the addition of $Ca(OH)_2$.

Answer

11.09

Due to their light sensitivity, mixtures of silver halides are used in fiber optics for medical lasers, in photochromic eyeglass lenses (glass lenses that automatically darken when exposed to sunlight), and—before the advent of digital photography—in photographic film. Even though AgCl ($K_{sp} = 1.6 \times 10^{-10}$), AgBr ($K_{sp} = 7.7 \times 10^{-13}$), and AgI ($K_{sp} = 8.3 \times 10^{-17}$) are each quite insoluble, we cannot prepare a homogeneous solid mixture of them by adding Ag^+ to a solution of Cl^-, Br^-, and I^-; essentially all of the AgI will precipitate before any of the other solid halides form because of its smaller value for K_{sp}. However, we can prepare a homogeneous mixture of the solids by slowly adding a solution of Cl^-, Br^-, and I^- to a solution of Ag^+.

When two anions form slightly soluble compounds with the same cation, or when two cations form slightly soluble compounds with the same anion, the less soluble compound (usually, the compound with the smaller K_{sp}) generally precipitates first when we add a precipitating agent to a solution containing both anions (or both cations). When the K_{sp} values of the two compounds differ by two orders of magnitude or more (e.g., 10^{-2} vs. 10^{-4}), almost all of the less soluble compound precipitates before any of the more soluble one does. This is an example of selective precipitation, where a reagent is added to a solution of dissolved ions causing one of the ions to precipitate out before the rest.

Determining if a Precipitate forms (The Ion Product): https://youtu.be/Naf7PoHPz8Y

Summary

A slightly soluble electrolyte begins to precipitate when the magnitude of the reaction quotient for the dissolution reaction exceeds the magnitude of the solubility product. Precipitation continues until the reaction quotient equals the solubility product. A reagent can be added to a solution of ions to allow one ion to selectively precipitate out of solution. The common ion effect can also play a role in precipitation reactions. In the presence of an ion in common with one of the ions in the solution, Le Chatelier's principle applies and more precipitate comes out of solution so that the molar solubility is reduced.

Glossary

common ion effect

effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base

molar solubility

solubility of a compound expressed in units of moles per liter (mol/L)

selective precipitation

process in which ions are separated using differences in their solubility with a given precipitating reagent

solubility product (K_{sp})

equilibrium constant for the dissolution of a slightly soluble electrolyte

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7.5: Fractional Precipitation

Learning Objectives

- Calculate ion concentrations to maintain a heterogeneous equilibrium.
- Calculate pH required to precipitate a metal hydroxide.
- Design experiments to separate metal ions in a solution of mixtures of metals.

A mixture of metal ions in a solution can be separated by precipitation with anions such as Cl^-, Br^-, SO_4^{2-}, CO_3^{2-}, S^{2-}, $Cr_2O_4^{2-}$, PO_4^{2-}, OH^- etc. When a metal ion or a group of metal ions form insoluble salts with a particular anion, they can be separated from others by precipitation. We can also separate the anions by precipitating them with appropriate metal ions. There are no definite dividing lines between **insoluble salts, sparingly soluble**, and **soluble salts**, but concentrations of their saturated solutions are small, medium, and large. Solubility products are usually listed for insoluble and sparingly soluble salts, but they are not given for soluble salts. Solubility products for soluble salts are very large.

What type of salts are usually soluble, sparingly soluble and insoluble? The following are some general guidelines, but these are not precise laws.

- All nitrates are soluble. The singly charged large NO_3^- ions form salts with high solubilities. So do ClO_4^-, ClO_3^-, NO_2^-, $HCOO^-$, and CH_3COO^-.
- All chlorides, bromides, and iodides are soluble except those of Ag^+, Hg_2^{2+}, and Pb^{2+}. CaF_2, BaF_2, and PbF_2 are also insoluble.
- All sulfates are soluble, except those of Ba^{2+}, Sr^{2+}, and Pb^{2+}. The doubly charged sulfates are usually less soluble than halides and nitrates.
- Most singly charge cations K^+, Na^+, NH_4^+ form soluble salts. However, $K_3Co(NO_2)_6$ and $(NH_4)_3Co(NO_2)_6$ are insoluble.

These are handy rules for us to have if we deal with salts often. On the other hand, solubility is an important physical property of a substance, and these properties are listed in handbooks.

Chemical Separation of Metal Ions

Formation of crystals from a saturated solution is a **heterogeneous equilibrium** phenomenon, and it can be applied to separate various chemicals or ions in a solution. When solubilities of two metal salts are very different, they can be separated by precipitation. The K_{sp} values for various salts are valuable information, and some data are given in Table E3. In the first two examples, we show how barium and strontium can be separated as chromate.

Example 7.5.1

The K_{sp} for strontium chromate is 3.6×10^{-5} and the K_{sp} for barium chromate is 1.2×10^{-10}. What concentration of potassium chromate will precipitate the maximum amount of either the barium or the strontium chromate from an equimolar 0.30 M solution of barium and strontium ions without precipitating the other?

Solution

Since the K_{sp} for barium chromate is smaller, we know that $BaCrO_4$ will form a precipitate first as $[CrO_4^{2-}]$ increases so that Q_{sp} for $BaCrO_4$ also increases from zero to K_{sp} of $BaCrO_4$, at which point, $BaCrO_4$ precipitates. As $[CrO_4^{2-}]$ increases, $[Ba^{2+}]$ decreases. Further increase of $[CrO_4^{2-}]$ till Q_{sp} for $SrCrO_4$ increases to K_{sp} of $SrCrO_4$; it then precipitates.

Let us write the equilibrium equations and data down to help us think. Let x be the concentration of chromate to precipitate Sr^{2+}, and y be that to precipitate Ba^{2+}:

$$SrCrO_4(s) \rightarrow Sr^{2+}(aq) + CrO_4^{2-}(aq)$$

According to the definition of K_{sp} we have we have $K_{sp} = (0.30)(x) = 3.6 \times 10^{-5}$. Solving for x gives

$$x = \frac{3.6 \times 10^{-5}}{0.30} = 1.2 \times 10^{-4} M$$

Further, let y be the concentration of chromate to precipitate precipitate Ba^{2+}:

$$\mathrm{BaCrO_4(s)} \rightarrow \mathrm{Ba^{2\,+}(aq)} + \mathrm{CrO_4^{2\,-}(aq)}$$

with $K_{sp} = (0.30)(y) = 1.2 \times 10^{-10}$. Solving for y gives

$$y = \frac{1.2 \times 10^{-10}}{0.30} = 4.0 \times 10^{-10}\ M$$

The K_{sp}'s for the two salts indicate $\mathrm{BaCrO_4}$ to be much less soluble, and it will precipitate before any $\mathrm{SrCrO_4}$ precipitates. If chromate concentration is maintained less than $1.2 \times 10^{-4}\,M$, then all $\mathrm{Sr^{2+}}$ ions will remain in the solution.

Discussion

In reality, controling the increase of $[\mathrm{CrO_4^{2-}}]$ is very difficult.

✓ Example 7.5.2

The K_{sp} for strontium chromate is 3.6×10^{-5} and the K_{sp} for barium chromate is 1.2×10^{-10}. Potassium chromate is added a small amount at a time to first precipitate $\mathrm{BaCrO_4}$. Calculate $[\mathrm{Ba^{2+}}]$ when the first trace of $\mathrm{SrCrO_4}$ precipitate starts to form in a solution that contains 0.30 M each of $\mathrm{Ba^{2+}}$ and $\mathrm{Sr^{2+}}$ ions.

Solution

From the solution given in Example $7.5.1$, $[\mathrm{CrO_4^{2-}}] = 3.6 \times 10^{-4}\ M$ when $\mathrm{SrCrO_4}$ starts to form. At this concentration, the $[\mathrm{Ba^{2+}}]$ is estimated at $3.6 \times 10^{-4} = 1.2 \times 10^{-10}$.

The K_{sp} of $\mathrm{BaCrO_4}$.

Thus,

$$[\mathrm{Ba^{2+}}] = 3.33 \times 10^{-7}\ M$$

Very small indeed, compared to 0.30. In the fresh precipitate of $\mathrm{SrCrO_4}$, the molar ratio of $\mathrm{SrCrO_4}$ to $\mathrm{BaCrO_4}$ is

$$\frac{0.30}{3.33 \times 10^{-7}} = 9.0 \times 10^{5}.$$

Hence, the amount of $\mathrm{Ba^{2+}}$ ion in the solid is only 1×10^{-6} (i.e., 1 ppm) of all metal ions, providing that all the solid was removed when

$$[\mathrm{CrO_4^{2\,-}}] = 3.6 \times 10^{-4}\,M.$$

Discussion

The calculation shown here indicates that the separation of Sr and Ba is pretty good. In practice, an impurity level of 1 ppm is a very small value.

✓ Example 7.5.3

What reagent should you use to separate silver and lead ions that are present in a solution? What data or information will be required for this task?

Solution

The K_{sp}'s for salts of silver and lead are required. We list the K_{sp}'s for chlorides and sulfates in a table here. These value are found in the Handbook Menu of our website as Salts K_{sp}.

Solutions to Example 17.6.3

Salt	K_{sp}	Salt	K_{sp}
AgCl	1.8×10^{-10}	$\mathrm{Ag_2SO_4}$	1.4×10^{-5}
$\mathrm{Hg_2Cl_2}$	1.3×10^{-18}	$\mathrm{BaSO_4}$	1.1×10^{-10}
$\mathrm{PbCl_2}$	1.7×10^{-5}	$\mathrm{CaSO_4}$	2.4×10^{-5}

Salt	K_{sp}	Salt	K_{sp}
		$PbSO_4$	6.3×10^{-7}
		$SrSO_4$	3.2×10^{-7}

Because the K_{sp}'s $AgCl$ and $PbCl_2$ are very different, chloride, Cl^-, apppears a good choice of negative ions for their separation.

The literature also indicates that $PbCl_2$ is rather soluble in warm water, and by heating the solution to 350 K (80°C), you can keep Pb^{2+} ions in solution and precipitate $AgCl$ as a solid. The solubility of $AgCl$ is very small even at high temperatures.

Discussion

Find more detailed information about the solubility of lead chloride as a function of temperature.

Can sulfate be used to separate silver and lead ions? Which one will form a precipitate first as the sulfate ion concentration increases? What is the $[Pb^{2+}]$ when Ag_2SO_4 begins to precipitate in a solution that contains 0.10 M Ag^+?

The Separation of Two Ions by a Difference in Solubility: The Separation of Two Ions by a Difference in Solubility(opens in new window) [youtu.be]

7.6: Solubility and pH

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:

$$\mathrm{A^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HA(aq)} \tag{7.6.1}$$

Because of the reaction described in Equation 7.6.1, 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

$$Q = \mathrm{[M^+][A^-]} \tag{7.6.2}$$

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:

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \tag{7.6.3}$$

with

$$K_{sp} = 5.61 \times 10^{-12} \tag{7.6.4}$$

When acid is added to a saturated solution that contains excess solid $Mg(OH)_2$, the following reaction occurs, removing OH^- from solution:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \tag{7.6.5}$$

The overall equation for the reaction of $Mg(OH)_2$ with acid is thus

$$Mg(OH)_{2(s)} + 2H^+(aq) \rightleftharpoons Mg^{2+}(aq) + 2H_2O(l) \tag{7.6.6}$$

As more acid is added to a suspension of $Mg(OH)_2$, the equilibrium shown in Equation 7.6.6 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:

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq) \tag{7.6.7}$$

with

$$K_{sp} = 3.45 \times 10^{-11} \tag{7.6.8}$$

When strong acid is added to a saturated solution of CaF_2, the following reaction occurs:

$$H^+(aq)+F^-(aq) \rightleftharpoons HF(aq) \tag{7.6.9}$$

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

$$CaF_{2(s)}+2H^+(aq) \rightarrow Ca^{2+}(aq)+2HF(aq) \tag{7.6.10}$$

Example $7.6.1$ 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 7.6.1

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 7.6.1

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 7.6.1:). 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:

$$\mathrm{CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)} \tag{7.6.11}$$

$$\mathrm{HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)} \tag{7.6.12}$$

$$\mathrm{Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)} \tag{7.6.13}$$

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 7.6.1:):

$$Ca^{2+}(aq) + 2HCO^-_{3(aq)} \rightleftharpoons CaCO_{3(s)} + CO_{2(g)} + H_2O(l) \tag{7.6.14}$$

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.

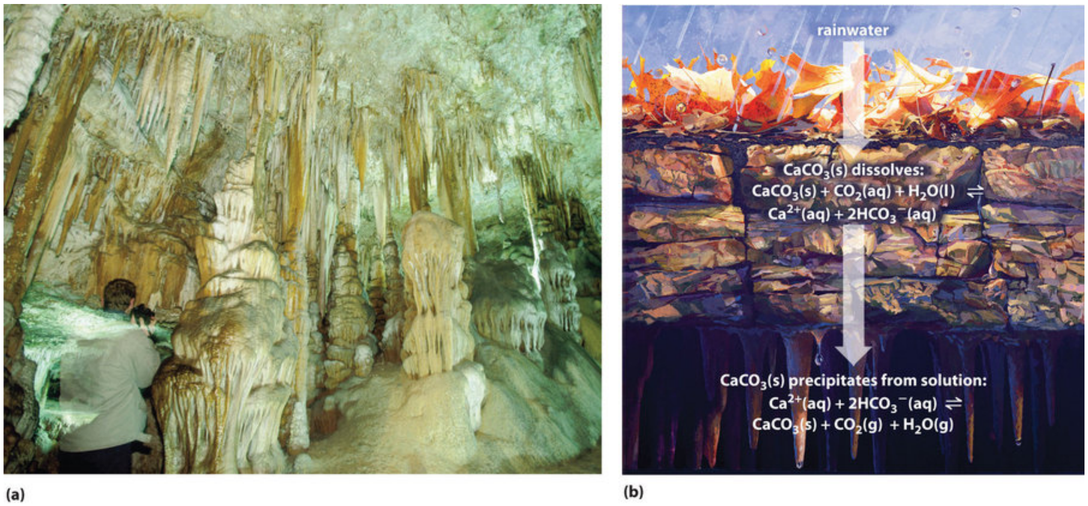


Figure 7.6.1: The Chemistry of Cave Formation. (a) This cave in Campanet, Mallorca, Spain, and its associated formations are examples of pH-dependent solubility equilibriums. (b) A cave forms when groundwater containing atmospheric CO_2, forming an acidic solution, dissolves limestone ($CaCO_3$) in a 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 7.6.11 and 7.6.12) finds its way into microscopic cracks in the limestone deposits, $CaCO_3$ dissolves in the acidic solution in the reverse direction of Equation 7.6.14. 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 7.6.14 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 7.6.2).

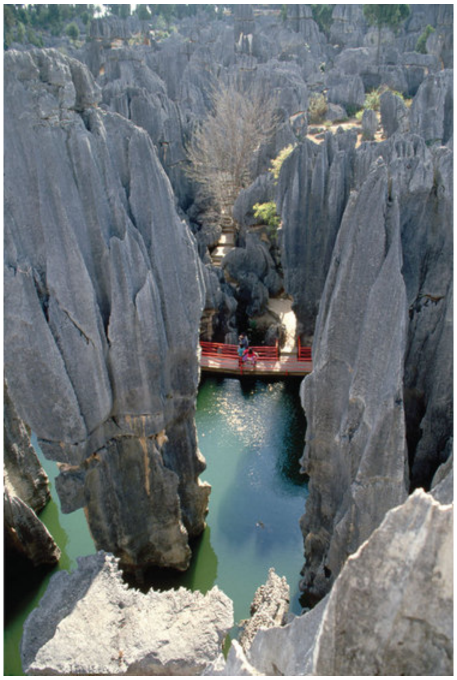


Figure 7.6.2: Solubility Equilbriain the Formation of Karst Landscapes. Landscapes such as the steep limestone pinnacles of the Stone Forest in Yunnan Province, China, are formed from the same process that produces caves and their associated formations.

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:

$$Cs_2O(s) + H_2O(l) \rightarrow 2Cs^+(aq) + 2OH^-(aq) \tag{7.6.15}$$

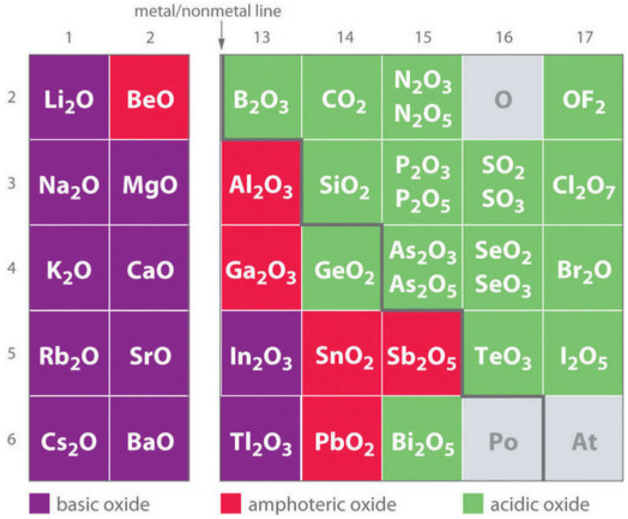
$$SO_{3(g)} + H_2O(l) \rightarrow H_2SO_{4(aq)} \tag{7.6.16}$$

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 ($MoO_4{}^{2-}$):

$$MoO_{3(s)} + 2OH^-(aq) \rightarrow MoO^{2-}_{4(aq)} + H_2O(l) \tag{7.6.17}$$



	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 7.6.3: 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 7.6.3, 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 7.6.1, 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:

$$\mathrm{Cr(OH)_3(s) + 3H^+(aq) \rightarrow \underset{violet}{Cr^{3+}(aq)} + 3H_2O(l)} \tag{7.6.18}$$

$$\mathrm{Cr(OH)_3(s) + OH^-(aq) \rightarrow \underset{green}{[Cr(OH)_4]^-(aq)}} \tag{7.6.19}$$

***Video 7.6.1**: 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 7.6.2

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 7.6.18 and 7.6.19 as 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 7.6.2

Copper(II) hydroxide, written as either $Cu(OH)_2$ or $CuO•H_2O$, 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 equlibria can be written as follows:

$$ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq) \tag{7.6.20}$$

with

$$K_{sp} = 1.6 \times 10^{-24} \tag{7.6.21}$$

and

$$CdS(s) \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq) \tag{7.6.22}$$

with

$$K_{sp} = 8.0 \times 10^{-27} \tag{7.6.23}$$

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:

$$K_{sp} = [Zn^{2+}][S^{2-}] \tag{7.6.24}$$

$$1.6 \times 10^{-24} = (0.0010\ M)[S^{2-}] \tag{7.6.25}$$

$$1.6 \times 10^{-21}\ M = [S^{2-}] \tag{7.6.26}$$

and

$$K_{sp} = [Cd^{2+}][S^{2-}] \tag{7.6.27}$$

$$8.0 \times 10^{-27} = (0.0010\ M)[S^{2-}] \tag{7.6.28}$$

$$8.0 \times 10^{-24}\ M = [S^{2-}] \tag{7.6.29}$$

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_2S contains 0.10 M H_2S at 20°C. The $pK_{a1}$for H_2S is 6.97, and pK_{a2} corresponding to the formation of $[S^{2-}]$ is 12.90. The equations for these reactions are as follows:

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq) \tag{7.6.30}$$

with

$$pK_{a1} = 6.97 \text{ and hence } K_{a1} = 1.1 \times 10^{-7} \tag{7.6.31}$$

$$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq) \tag{7.6.32}$$

with

$$pK_{a2} = 12.90 \text{ and hence } K_{a2} = 1.3 \times 10^{-13} \tag{7.6.33}$$

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:

$$K_{\text{a1}} = 1.1 \times 10^{-7} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = \frac{x^2}{0.10 \text{ M}} \tag{7.6.34}$$

$$x = 1.1 \times 10^{-4} \text{ M} = [\text{H}^+] = [\text{HS}^-]$$

Substituting this value for $[H^+]$ and $[HS^-]$ into the equation for K_{a2},

$$K_{\text{a2}} = 1.3 \times 10^{-13} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} = \frac{(1.1 \times 10^{-4} \text{ M})x}{1.1 \times 10^{-4} \text{ M}} = x = [\text{S}^{2-}] \tag{7.6.35}$$

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 7.6.33 to the left. The overall equation for the dissociation of H_2S is as follows:

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq) \tag{7.6.36}$$

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:

$$K = K_{\text{a1}}K_{\text{a2}} = (1.1 \times 10^{-7})(1.3 \times 10^{-13}) = 1.4 \times 10^{-20} = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]} \tag{7.6.37}$$

$$[\text{H}^+]^2 = \frac{K[\text{H}_2\text{S}]}{[\text{S}^{2-}]} = \frac{(1.4 \times 10^{-20})(0.10 \text{ M})}{1.6 \times 10^{-21} \text{ M}} = 0.88 \tag{7.6.38}$$

$$[\text{H}^+] = 0.94 \tag{7.6.39}$$

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 7.6.3

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:

$$HO_2CCO_2H(aq) \rightleftharpoons 2H^+(aq) + C_2O^{2-}_{4(aq)} \tag{7.6.40}$$

$$K = K_{a1}K_{a2} = (10^{-1.25})(10^{-3.81}) = 10^{-5.06} = 8.7\times10^{-6}$$

Substituting the desired oxalate concentration into the equilibrium constant expression,

$$8.7 \times 10^{-6} = \frac{[\mathrm{H^+}]^2[\mathrm{ox^{2-}}]}{[\mathrm{HO_2CCO_2H}]} = \frac{[\mathrm{H^+}]^2(2.32 \times 10^{-7})}{1.0} \tag{7.6.41}$$

$$[\mathrm{H^+}] = 6.1\ \mathrm{M} \tag{7.6.42}$$

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 7.6.3

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

7.7: Equilibria Involving Complex Ions

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 7.7.1. 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 7.7.1: 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 https://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:

$$\mathrm{Cu^{2+}(aq)} + \mathrm{NH_{3(aq)}} \rightleftharpoons [\mathrm{Cu(NH_3)}]^{2+}_{\mathrm{(aq)}} \quad K_1 \tag{7.7.1}$$

$$[\mathrm{Cu(NH_3)}]^{2+}_{\mathrm{(aq)}} + \mathrm{NH_{3(aq)}} \rightleftharpoons [\mathrm{Cu(NH_3)_2}]^{2+}_{\mathrm{(aq)}} \quad K_2 \tag{7.7.2}$$

$$[\mathrm{Cu(NH_3)_2}]^{2+}_{\mathrm{(aq)}} + \mathrm{NH_{3(aq)}} \rightleftharpoons [\mathrm{Cu(NH_3)_3}]^{2+}_{\mathrm{(aq)}} \quad K_3 \tag{7.7.3}$$

$$[\mathrm{Cu(NH_3)_3}]^{2+}_{\mathrm{(aq)}} + \mathrm{NH_{3(aq)}} \rightleftharpoons [\mathrm{Cu(NH_3)_4}]^{2+}_{\mathrm{(aq)}} \quad K_4 \tag{7.7.4}$$

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.

$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \tag{7.7.5}$$

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:

$$K_\mathrm{f} = \frac{\left[[\mathrm{Cu(NH_3)_4}]^{2+}\right]}{[\mathrm{Cu^{2+}}][\mathrm{NH_3}]^4} = 2.1 \times 10^{13} = K_1 K_2 K_3 K_4 \tag{7.7.6}$$

> *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 7.7.1.

Table 7.7.1: Formation Constants for Selected Complex Ions in Aqueous Solution*

	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 7.7.1

If 12.5 g of $Cu(NO_3)_2•6H_2O$ 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 7.7.5 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 7.7.6) 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 7.7.5. 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:

$$12.5\ \cancel{g}\ \mathrm{Cu(NO_3)_2\cdot 6H_2O}\left(\frac{1\ \mathrm{mol}}{295.65\ \cancel{g}}\right)\left(\frac{1}{500\ \cancel{mL}}\right)\left(\frac{1000\ \cancel{mL}}{1\ \mathrm{L}}\right)=0.0846\ \mathrm{M} \tag{7.7.7}$$

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.

$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$

	$[Cu^{2+}]$	**$[NH_3]$**	**$[[Cu(NH_3)_4]^{2+}]$**
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 7.7.6) and assuming that $x << 0.0846$, which allows us to remove x from the sum and difference,

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{0.0846 - x}{x(0.66 + 4x)^4} \approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13} \tag{7.7.8}$$

$$x = 2.1 \times 10^{-14} \tag{7.7.9}$$

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 7.7.1

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.

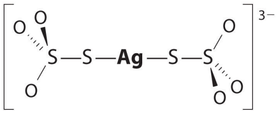
The reaction for the dissolution of silver bromide is as follows:

$$AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)} \tag{7.7.10}$$

with

$$K_{sp} = 5.35 \times 10^{-13} \text{ at } 25^\circ\text{C} \tag{7.7.11}$$

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:

$$Ag^+_{(aq)} + 2S_2O^{2-}_{3(aq)} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}_{(aq)} \tag{7.7.12}$$

with

$$K_f = 2.9 \times 10^{13} \tag{7.7.13}$$

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:

$$\mathrm{AgBr(s)} \rightleftharpoons \mathrm{Ag^+(aq) + Br^-(aq)} \quad K_{\mathrm{sp}} = 5.35 \times 10^{-13} \tag{7.7.14}$$

$$\mathrm{Ag^+(aq) + 2S_2O_3^{2-}(aq)} \rightleftharpoons \mathrm{[Ag(S_2O_3)_2]^{3-}(aq)} \quad K_{\mathrm{f}} = 2.9 \times 10^{13} \tag{7.7.15}$$

$$\mathrm{AgBr(s) + 2S_2O_3^{2-}(aq)} \rightleftharpoons \mathrm{[Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)} \quad K = K_{\mathrm{sp}}K_{\mathrm{f}} = 15 \tag{7.7.16}$$

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 7.7.2

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:

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)} \quad K_{sp} = 1.77\times10^{-10} \tag{7.7.17}$$

$$\mathrm{Ag^+(aq)} + 2\mathrm{Cl^-} \rightleftharpoons [\mathrm{AgCl_2}]^- \quad K_f = 1.1\times10^5 \tag{7.7.18}$$

$$\mathrm{AgCl(s)} + \mathrm{Cl^-} \rightleftharpoons [\mathrm{AgCl_2}]^- \quad K = K_{sp}K_f = 1.9\times10^{-5} \tag{7.7.19}$$

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 $x << 1.0$,

$$K = \frac{[\mathrm{AgCl_2^-}]}{[\mathrm{Cl^-}]} = \frac{x}{1.0 - x} \approx 1.9\times10^{-5} = x$$

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 7.7.2

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

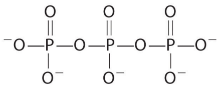
$$K_{sp} = 2.9 \times 10^{-29} \text{ for } HgI_2 \text{ and } K_f = 6.8 \times 10^{29} \text{ for } [HgI_4]^{2-}.$$

Answer

a. 1.9×10^{-10} M
b. 1.4 M

Solubility of Complex Ions: https://youtu.be/f4pkKDg2XTA

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:



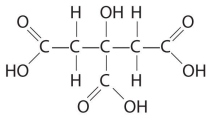
triphosphate

$$Ca^{2+}_{(aq)} + O_3POPO^{4-}_{4(aq)} \rightleftharpoons [Ca(O_3POPO_3)]^{2-}_{(aq)} \tag{7.7.20}$$

with

$$K_f = 4 \times 10^4 \tag{7.7.21}$$

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.



Citric acid,
a hydroxy polycarboxylic acid

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.

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 7.7.2). 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.

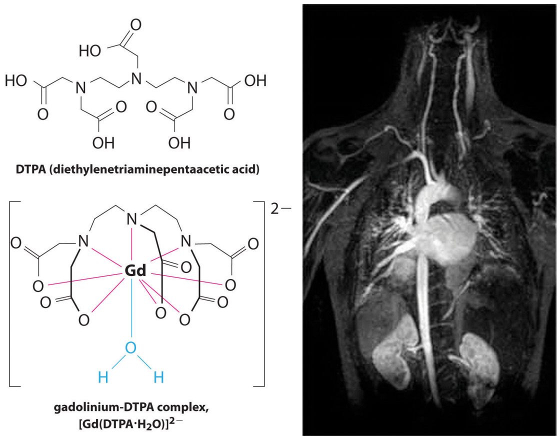


Figure $7.7.2$: An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

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.

7.8: Qualitative Cation Analysis

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 7.8.1.

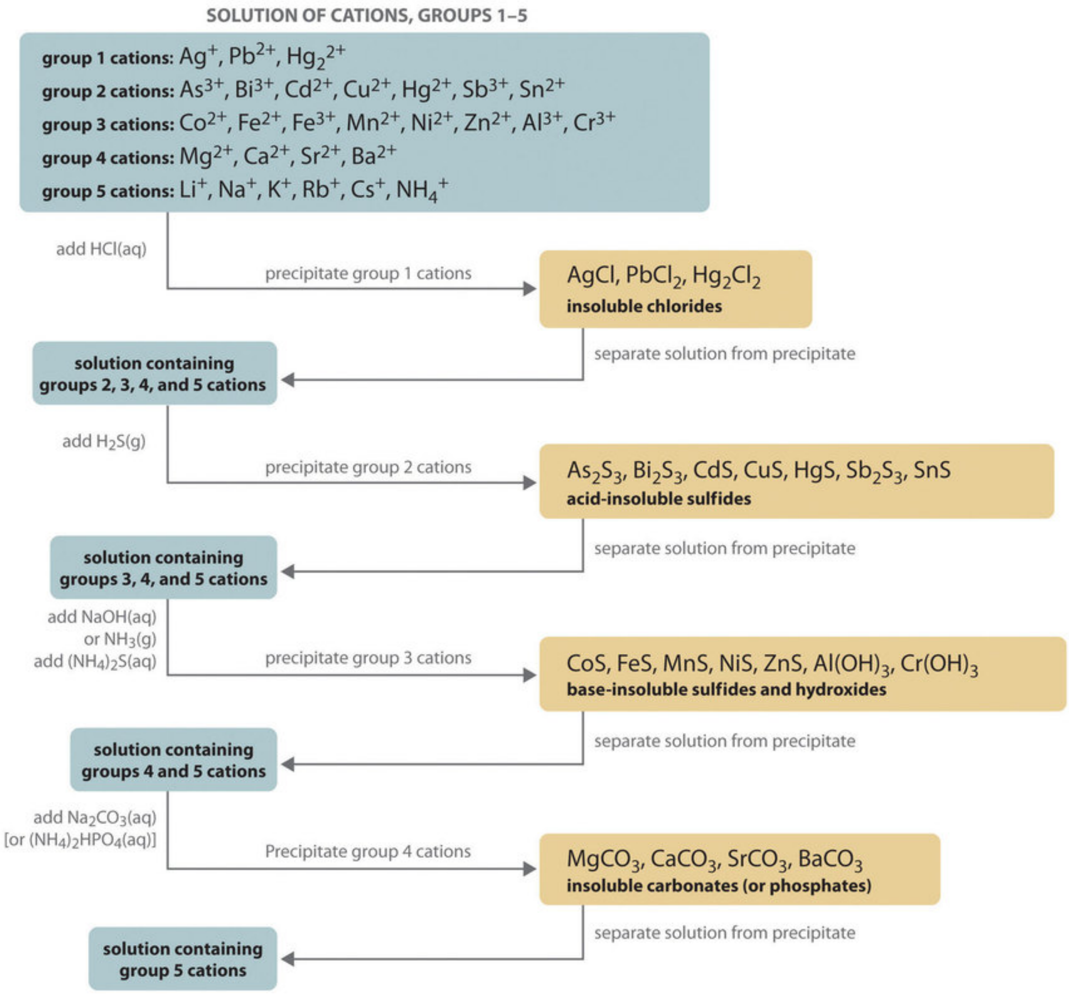


Figure 7.8.1: Steps in a Typical Qualitative Analysis Scheme for a Solution That Contains Several Metal Ions

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 $7.8.2$).

Figure $7.8.2$: 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.

7.9: Equilibria of Other Reaction Classes (Exercises)

7.9.1: **Precipitation and Dissolution**

1. How do the concentrations of Ag^+ and CrO2−4CrO42− in a saturated solution above 1.0 g of solid Ag_2CrO_4 change when 100 g of solid Ag_2CrO_4 is added to the system? Explain.

Answer

There is no change. A solid has an activity of 1 whether there is a little or a lot.

2. How do the concentrations of Pb^{2+} and S^{2-} change when K_2S is added to a saturated solution of PbS?

3. What additional information do we need to answer the following question: How is the equilibrium of solid silver bromide with a saturated solution of its ions affected when the temperature is raised?

Answer

The solubility of silver bromide at the new temperature must be known. Normally the solubility increases and some of the solid silver bromide will dissolve.

4.Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: $CoSO_3$, CuI, $PbCO_3$, $PbCl_2$, Tl_2S, $KClO_4$?

5. Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: AgCl, $BaSO_4$, CaF_2, Hg_2I_2, $MnCO_3$, ZnS, PbS?

Answer

CaF_2, $MnCO_3$, and ZnS

6. Write the ionic equation for dissolution and the solubility product (K_{sp}) expression for each of the following slightly soluble ionic compounds:

1. $PbCl_2$
2. Ag_2S
3. $Sr_3(PO_4)_2$
4. $SrSO_4$

7. Write the ionic equation for the dissolution and the K_{sp} expression for each of the following slightly soluble ionic compounds:

a. LaF_3

b. $CaCO_3$

c. Ag_2SO_4

d. $Pb(OH)_2$

Answer

a. $LaF_3(s)\rightleftharpoons La^{3+}(aq)+3F^-(aq)$ $Ksp=[La^{3+}][F^-]^3$;
b. $CaCO_3(s)\rightleftharpoons Ca^{2+}(aq)+CO_3{}^{2-}(aq)$ $Ksp=[Ca^{2+}][CO_3{}^{2-}]$;
c. $Ag_2SO_4(s)\rightleftharpoons 2Ag^+(aq)+SO_4{}^{2-}(aq)$ $Ksp=[Ag^+]^2[SO_4{}^{2-}]$;
d. $Pb(OH)_2(s)\rightleftharpoons Pb^{2+}(aq)+2OH^-(aq)$ $Ksp=[Pb^{2+}][OH^-]^2$

8. The *Handbook of Chemistry and Physics* gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.

a. $BaSiF_6$, 0.026 g/100 mL (contains $SiF_6{}^{2-}$ ions)

b. $Ce(IO_3)_4$, 1.5×10^{-2} g/100 mL

c. $Gd_2(SO_4)_3$, 3.98 g/100 mL

d. $(NH_4)_2PtBr_6$, 0.59 g/100 mL (contains PtBr2−6PtBr62− ions)

9. The *Handbook of Chemistry and Physics* gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.

a. $BaSeO_4$, 0.0118 g/100 mL

b. $Ba(BrO_3)_2•H_2O$, 0.30 g/100 mL

c. $NH_4MgAsO_4•6H_2O$, 0.038 g/100 mL

d. $La_2(MoO_4)_3$, 0.00179 g/100 mL

Answer

a. 1.77×10^{-7}; b. 1.6×10^{-6}; c. 2.2×10^{-9}; d. 7.91×10^{-22}

10. Use solubility products and predict which of the following salts is the most soluble, in terms of moles per liter, in pure water: CaF_2, Hg_2Cl_2, PbI_2, or $Sn(OH)_2$.

11. Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:

a. $KHC_4H_4O_6$

b. PbI_2

c. $Ag_4[Fe(CN)_6]$, a salt containing the Fe(CN)−4Fe(CN)4− ion

d. Hg_2I_2

Answer

a. 2×10^{-2} *M*; b. 1.3×10^{-3} *M*; c. 2.27×10^{-9} *M*; d. 2.2×10^{-10} *M*

12. Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:

a. Ag_2SO_4

b. $PbBr_2$

c. AgI

d. $CaC_2O_4•H_2O$

13. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.

a. AgCl(*s*) in 0.025 *M* NaCl

b. CaF_2(*s*) in 0.00133 *M* KF

c. Ag_2SO_4(*s*) in 0.500 L of a solution containing 19.50 g of K_2SO_4

d. $Zn(OH)_2$(*s*) in a solution buffered at a pH of 11.45

Answer

a. 7.2×10^{-9} *M* = $[Ag^+]$, $[Cl^-]$ = 0.025 *M*

Check: 7.2×10−9M0.025M×100%=2.9×10−5%7.2×10−9M0.025M×100%=2.9×10−5%, an insignificant change.

b. 2.2×10^{-5} *M* = $[Ca^{2+}]$, $[F^-]$ = 0.0013 *M*

Check: 2.25×10−5M0.00133M×100%=1.69%2.25×10−5M0.00133M×100%=1.69%. This value is less than 5% and can be ignored.

c. 0.2238 M = [SO2−4][SO42−]; [Ag^+] = 2.30 × 10^{-9} M

Check: 1.15×10−90.2238×100%=5.14×10−71.15×10−90.2238×100%=5.14×10−7; the condition is satisfied.

d. [OH^-] = 2.8 × 10^{-3} M; 5.7 × 10^{-12} M = [Zn^{2+}]

Check: 5.7×10−122.8×10−3×100%=2.0×10−7%5.7×10−122.8×10−3×100%=2.0×10−7%; x is less than 5% of [OH^-] and is, therefore, negligible.

14. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.

a. TlCl(s) in 1.250 M HCl

b. PbI_2(s) in 0.0355 M CaI_2

c. Ag_2CrO_4(s) in 0.225 L of a solution containing 0.856 g of K_2CrO_4

d. $Cd(OH)_2$(s) in a solution buffered at a pH of 10.995

15. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that it is not appropriate to neglect the changes in the initial concentrations of the common ions.

a. TlCl(s) in 0.025 M $TlNO_3$

b. BaF_2(s) in 0.0313 M KF

c. MgC_2O_4 in 2.250 L of a solution containing 8.156 g of $Mg(NO_3)_2$

d. $Ca(OH)_2$(s) in an unbuffered solution initially with a pH of 12.700

Answer

a. [Cl^-] = 7.6 × 10^{-3} M

Check: 7.6×10^{-3} / 0.025 × 100%=30%

This value is too large to drop x. Therefore solve by using the quadratic equation:

[Ti^+] = 3.1 × 10^{-2} M; [Cl^-] = 6.1 × 10^{-3}

b. [Ba^{2+}] = 1.7 × 10^{-3} M

Check: 1.7×10^{-3} / 0.0313×100%=5.5%

This value is too large to drop x, and the entire equation must be solved.

[Ba^{2+}] = 1.6 × 10^{-3} M; [F^-] = 0.0329 M;

c. $Mg(NO_3)_2$ = 0.02444 M

[$C_2O_4^{2-}$]=3.5×10^{-3}

Check: 3.5×10^{-3} / 0.02444 × 100%=14%

This value is greater than 5%, so the quadratic equation must be used:

[$C_2O_4^{2-}$]=3.5×10^{-3} M; [Mg^{2+}] = 0.0275 M;

d. [Ca^{2+}] = 2.8 × 10^{-3} M, [OH^-] = 0.053 × 10^{-2} M

16. Explain why the changes in concentrations of the common ions in the previous problem cannot be neglected.

Answer

The changes in concentration are greater than 5% and thus exceed the maximum value for disregarding the change.

17. Calculate the solubility of aluminum hydroxide, $Al(OH)_3$, in a solution buffered at pH 11.00.

18. Refer to Appendix J for solubility products for calcium salts. Determine which of the calcium salts listed is most soluble in moles per liter and which is most soluble in grams per liter.

Answer

$CaSO_4·2H_2O$ is the most soluble Ca salt in mol/L, and it is also the most soluble Ca salt in g/L.

19. Most barium compounds are very poisonous; however, barium sulfate is often administered internally as an aid in the X-ray examination of the lower intestinal tract. This use of $BaSO_4$ is possible because of its low solubility. Calculate the molar solubility of $BaSO_4$ and the mass of barium present in 1.00 L of water saturated with $BaSO_4$.

20. Public Health Service standards for drinking water set a maximum of 250 mg/L (2.60×10^{-3} *M*) of SO_4^{2-} because of its cathartic action (it is a laxative). Does natural water that is saturated with $CaSO_4$ (“gyp” water) as a result or passing through soil containing gypsum, $CaSO_4•2H_2O$, meet these standards? What is $[SO_4^{2-}]$ in such water?

Answer

4.9×10^{-3} *M* = $[SO_4^{2-}]$= $[Ca^{2+}]$; Since this concentration is higher than 2.60×10^{-3} *M*, “gyp” water does not meet the standards.

21. Perform the following calculations:

1. Calculate $[Ag^+]$ in a saturated aqueous solution of AgBr.
2. What will $[Ag^+]$ be when enough KBr has been added to make $[Br^-]$ = 0.050 *M*?
3. What will $[Br^-]$ be when enough $AgNO_3$ has been added to make $[Ag^+]$ = 0.020 *M*?

22. The solubility product of $CaSO_4•2H_2O$ is 2.4×10^{-5}. What mass of this salt will dissolve in 1.0 L of 0.010 *M* SO_4^{2-}?

Answer

Mass ($CaSO_4•2H_2O$) = 0.34 g/L

23. Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a saturated solution of each of the following (see Table E3 for solubility products).

a. TlCl

b. BaF_2

c. Ag_2CrO_4

d. $CaC_2O_4•H_2O$

e. the mineral anglesite, $PbSO_4$

24. Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a saturated solution of each of the following (see Table E3 for solubility products).

a. AgI

b. Ag_2SO_4

c. $Mn(OH)_2$

d. $Sr(OH)_2•8H_2O$

e. the mineral brucite, $Mg(OH)_2$

Answer

$[Ag^+] = [I^-] = 1.2 \times 10^{-8}$ *M*; $[Ag^+] = 2.86 \times 10^{-2}$ *M*, [SO2−4][SO42−] = 1.43×10^{-2} *M*; $[Mn^{2+}] = 2.2 \times 10^{-5}$ *M*, $[OH^-] = 4.5 \times 10^{-5}$ *M*; $[Sr^{2+}] = 4.3 \times 10^{-2}$ *M*, $[OH^-] = 8.6 \times 10^{-2}$ *M*; $[Mg^{2+}] = 1.6 \times 10^{-4}$ *M*, $[OH^-] = 3.1 \times 10^{-4}$ *M*.

25. The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:

1. AgBr: $[Ag^+] = 5.7 \times 10^{-7}$ *M*, $[Br^-] = 5.7 \times 10^{-7}$ *M*
2. $CaCO_3$: $[Ca^{2+}] = 5.3 \times 10^{-3}$ *M*, [CO 3 2−] = 9.0×10^{-7} *M*
3. PbF_2: $[Pb^{2+}] = 2.1 \times 10^{-3}$ *M*, $[F^-] = 4.2 \times 10^{-3}$ *M*
4. Ag_2CrO_4: $[Ag^+] = 5.3 \times 10^{-5}$ *M*, 3.2×10^{-3} *M*
5. InF_3: $[In^{3+}] = 2.3 \times 10^{-3}$ *M*, $[F^-] = 7.0 \times 10^{-3}$ *M*

26. The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:

1. TlCl: $[Tl^+] = 1.21 \times 10^{-2}$ *M*, $[Cl^-] = 1.2 \times 10^{-2}$ *M*
2. $Ce(IO_3)_4$: $[Ce^{4+}] = 1.8 \times 10^{-4}$ *M*, [IO−3][IO3−] = 2.6×10^{-13} *M*
3. $Gd_2(SO_4)_3$: $[Gd^{3+}] = 0.132$ *M*, [SO2−4][SO42−] = 0.198 *M*
4. Ag_2SO_4: $[Ag^+] = 2.40 \times 10^{-2}$ *M*, [SO2−4][SO42−] = 2.05×10^{-2} *M*
5. $BaSO_4$: $[Ba^{2+}] = 0.500$ *M*, [SO2−4][SO42−] = 2.16×10^{-10} *M*

Answer

2.0×10^{-4}; 5.1×10^{-17}; 1.35×10^{-4}; 1.18×10^{-5}; 1.08×10^{-10}

27. Which of the following compounds precipitates from a solution that has the concentrations indicated? (See Table E3 for K_{sp} values.)

1. $KClO_4$: $[K^+] = 0.01$ *M*, [ClO−4][ClO4−] = 0.01 *M*
2. K_2PtCl_6: $[K^+] = 0.01$ *M*, [PtCl2−6][PtCl62−] = 0.01 *M*
3. PbI_2: $[Pb^{2+}] = 0.003$ *M*, $[I^-] = 1.3 \times 10^{-3}$ *M*
4. Ag_2S: $[Ag^+] = 1 \times 10^{-10}$ *M*, $[S^{2-}] = 1 \times 10^{-13}$ *M*

28. Which of the following compounds precipitates from a solution that has the concentrations indicated? (See Table E3 for K_{sp} values.)

a. $CaCO_3$: $[Ca^{2+}] = 0.003$ *M*, [CO2−3][CO32−] = 0.003 *M*

b. $Co(OH)_2$: $[Co^{2+}] = 0.01$ *M*, $[OH^-] = 1 \times 10^{-7}$ *M*

c. $CaHPO_4$: $[Ca^{2+}] = 0.01$ *M*, [HPO2−4][HPO42−] = 2×10^{-6} *M*

d. $Pb_3(PO_4)_2$: $[Pb^{2+}] = 0.01$ *M*, [PO3−4][PO43−] = 1×10^{-13} *M*

Answer

a. $CaCO_3$ does precipitate; b. The compound does not precipitate; c. The compound does not precipitate; d. The compound precipitates.

29. Calculate the concentration of Tl^+ when TlCl just begins to precipitate from a solution that is 0.0250 *M* in Cl^-.

30. Calculate the concentration of sulfate ion when $BaSO_4$ just begins to precipitate from a solution that is 0.0758 *M* in Ba^{2+}.

Answer

1.42×10^{-9} M

31. Calculate the concentration of Sr^{2+} when SrF_2 starts to precipitate from a solution that is 0.0025 *M* in F^-.

32. Calculate the concentration of PO3−4PO43− when Ag_3PO_4 starts to precipitate from a solution that is 0.0125 *M* in Ag^+.

Answer

9.2×10^{-13} *M*

33. Calculate the concentration of F^- required to begin precipitation of CaF_2 in a solution that is 0.010 *M* in Ca^{2+}.

34. Calculate the concentration of Ag^+ required to begin precipitation of Ag_2CO_3 in a solution that is 2.50×10^{-6} *M* in CO2−3CO32−.

Answer

$[Ag^+] = 1.8 \times 10^{-3}$ *M*

35. What $[Ag^+]$ is required to reduce [CO2−3][CO32−] to 8.2×10^{-4} *M* by precipitation of Ag_2CO_3?

36. What $[F^-]$ is required to reduce $[Ca^{2+}]$ to 1.0×10^{-4} *M* by precipitation of CaF_2?

Answer

6.2×10^{-4} M

37. volume of 0.800 L of a 2×10^{-4}-*M* $Ba(NO_3)_2$ solution is added to 0.200 L of 5×10^{-4} *M* Li_2SO_4. Does $BaSO_4$ precipitate? Explain your answer.

38. Perform these calculations for nickel(II) carbonate.

1. With what volume of water must a precipitate containing $NiCO_3$ be washed to dissolve 0.100 g of this compound? Assume that the wash water becomes saturated with $NiCO_3$ ($K_{sp} = 1.36 \times 10^{-7}$).
2. If the $NiCO_3$ were a contaminant in a sample of $CoCO_3$ ($K_{sp} = 1.0 \times 10^{-12}$), what mass of $CoCO_3$ would have been lost? Keep in mind that both $NiCO_3$ and $CoCO_3$ dissolve in the same solution.

Answer

2.28 L; 7.3×10^{-7} g

39. Iron concentrations greater than 5.4×10^{-6} *M* in water used for laundry purposes can cause staining. What $[OH^-]$ is required to reduce $[Fe^{2+}]$ to this level by precipitation of $Fe(OH)_2$?

40. A solution is 0.010 *M* in both Cu^{2+} and Cd^{2+}. What percentage of Cd^{2+} remains in the solution when 99.9% of the Cu^{2+} has been precipitated as CuS by adding sulfide?

Answer

100% of it is dissolved

41. A solution is 0.15 *M* in both Pb^{2+} and Ag^{+}. If Cl^- is added to this solution, what is $[Ag^+]$ when $PbCl_2$ begins to precipitate?

42. What reagent might be used to separate the ions in each of the following mixtures, which are 0.1 *M* with respect to each ion? In some cases it may be necessary to control the pH. (Hint: Consider the K_{sp} values given in Appendix J.)

a. Hg2+2Hg22+ and Cu^{2+}

b. SO2−4SO42− and Cl^-

c. Hg^{2+} and Co^{2+}

d. Zn^{2+} and Sr^{2+}

e. Ba^{2+} and Mg^{2+}

f. CO2−3CO32− and OH^-

Answer

a. Hg2+2Hg22+ and Cu^{2+}: Add SO2−4SO42−.
b. SO2−4SO42− and Cl^-: Add Ba^{2+}.
c. Hg^{2+} and Co^{2+}: Add S^{2-}.
d. Zn^{2+} an Sr^{2+}: Add OH^- until $[OH^-] = 0.050$ *M*.
e. Ba^{2+} and Mg^{2+}: Add SO2−4SO42−
f. CO2−3CO32− and OH^-: Add Ba^{2+}.

43. A solution contains 1.0×10^{-5} mol of KBr and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgBr or solid AgCl?

44. A solution contains 1.0×10^{-2} mol of KI and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgI or solid AgCl?

Answer

AgI will precipitate first.

45. The calcium ions in human blood serum are necessary for coagulation. Potassium oxalate, $K_2C_2O_4$, is used as an anticoagulant when a blood sample is drawn for laboratory tests because it removes the calcium as a precipitate of $CaC_2O_4{\bullet}H_2O$. It is necessary

to remove all but 1.0% of the Ca^{2+} in serum in order to prevent coagulation. If normal blood serum with a buffered pH of 7.40 contains 9.5 mg of Ca^{2+} per 100 mL of serum, what mass of $K_2C_2O_4$ is required to prevent the coagulation of a 10 mL blood sample that is 55% serum by volume? (All volumes are accurate to two significant figures. Note that the volume of serum in a 10-mL blood sample is 5.5 mL. Assume that the K_{sp} value for CaC_2O_4 in serum is the same as in water.)

46. About 50% of urinary calculi (kidney stones) consist of calcium phosphate, $Ca_3(PO_4)_2$. The normal mid range calcium content excreted in the urine is 0.10 g of Ca^{2+} per day. The normal mid range amount of urine passed may be taken as 1.4 L per day. What is the maximum concentration of phosphate ion that urine can contain before a calculus begins to form?

Answer

4×10^{-9} *M*

47. The pH of normal urine is 6.30, and the total phosphate concentration ([PO3−4][PO43−] + [HPO2−4][HPO42−] + [H2PO−4][H2PO4−] + [H_3PO_4]) is 0.020 *M*. What is the minimum concentration of Ca^{2+} necessary to induce kidney stone formation? (See Exercise for additional information.)

48. Magnesium metal (a component of alloys used in aircraft and a reducing agent used in the production of uranium, titanium, and other active metals) is isolated from sea water by the following sequence of reactions:

Mg2+(aq)+Ca(OH)2(aq)⟶Mg(OH)2(s)+Ca2+(aq)

Mg(OH)2(s)+2HCl(aq)⟶MgCl2(s)+2H2O(l)

MgCl2(l)→Mg(s)+Cl2(g) (electrolysis)

49. Sea water has a density of 1.026 g/cm^3 and contains 1272 parts per million of magnesium as $Mg^{2+}(aq)$ by mass. What mass, in kilograms, of $Ca(OH)_2$ is required to precipitate 99.9% of the magnesium in 1.00×10^3 L of sea water?

Answer

3.99 kg

50. Hydrogen sulfide is bubbled into a solution that is 0.10 *M* in both Pb^{2+} and Fe^{2+} and 0.30 *M* in HCl. After the solution has come to equilibrium it is saturated with H_2S ($[H_2S] = 0.10$ *M*). What concentrations of Pb^{2+} and Fe^{2+} remain in the solution? For a saturated solution of H_2S we can use the equilibrium:

H2S(aq)+2H2O(l)⇌2H3O+(aq)+S2−(aq) K=1.0×10−26

(Hint: The [H3O+] changes as metal sulfides precipitate.)

51. Perform the following calculations involving concentrations of iodate ions:

1. The iodate ion concentration of a saturated solution of $La(IO_3)_3$ was found to be 3.1×10^{-3} mol/L. Find the K_{sp}.
2. Find the concentration of iodate ions in a saturated solution of $Cu(IO_3)_2$ ($K_{sp} = 7.4 \times 10^{-8}$).

Answer

3.1×10^{-11}; $[Cu^{2+}] = 2.6 \times 10^{-3}$; [IO−3][IO3−] = 5.3×10^{-3}

52. Calculate the molar solubility of AgBr in 0.035 *M* NaBr ($K_{sp} = 5 \times 10^{-13}$).

53. How many grams of $Pb(OH)_2$ will dissolve in 500 mL of a 0.050-*M* $PbCl_2$ solution ($K_{sp} = 1.2 \times 10^{-15}$)?

Answer

1.8×10^{-5} g $Pb(OH)_2$

54. Use the simulation from the earlier Link to Learning to complete the following exercise:. Using 0.01 g CaF_2, give the K_{sp} values found in a 0.2-*M* solution of each of the salts. Discuss why the values change as you change soluble salts.

55. How many grams of Milk of Magnesia, $Mg(OH)_2$ (*s*) (58.3 g/mol), would be soluble in 200 mL of water. $K_{sp} = 7.1 \times 10^{-12}$. Include the ionic reaction and the expression for K_{sp} in your answer. ($K_w = 1 \times 10^{-14} = [H_3O^+][OH^-]$)

Answer

Mg(OH)2(s)⇌Mg2+2OH−

Ksp=[Mg2+][OH−]2

1.14×10^{-3} g $Mg(OH)_2$

56. Two hypothetical salts, LM_2 and LQ, have the same molar solubility in H_2O. If K_{sp} for LM_2 is 3.20×10^{-5}, what is the K_{sp} value for LQ?

57. Which of the following carbonates will form first? Which of the following will form last? Explain.

1. MgCO3Ksp=3.5×10−8
2. CaCO3Ksp=4.2×10−7
3. SrCO3Ksp=3.9×10−9
4. BaCO3Ksp=4.4×10−5
5. MnCO3Ksp=5.1×10−9

Answer

$SrCO_3$ will form first, since it has the smallest K_{sp} value it is the least soluble. $BaCO_3$ will be the last to precipitate, it has the largest K_{sp} value.

58. How many grams of $Zn(CN)_2(s)$ (117.44 g/mol) would be soluble in 100 mL of H_2O? Include the balanced reaction and the expression for K_{sp} in your answer. The K_{sp} value for $Zn(CN)_2(s)$ is 3.0×10^{-16}.

7.9.2: Lewis Acids and Bases

59. Under what circumstances, if any, does a sample of solid AgCl completely dissolve in pure water?

Answer

when the amount of solid is so small that a saturated solution is not produced

60. Explain why the addition of NH_3 or HNO_3 to a saturated solution of Ag_2CO_3 in contact with solid Ag_2CO_3 increases the solubility of the solid.

61. Calculate the cadmium ion concentration, $[Cd^{2+}]$, in a solution prepared by mixing 0.100 L of 0.0100 M $Cd(NO_3)_2$ with 1.150 L of 0.100 $NH_3(aq)$.

Answer

2.35×10^{-4} M

62. Explain why addition of NH_3 or HNO_3 to a saturated solution of $Cu(OH)_2$ in contact with solid $Cu(OH)_2$ increases the solubility of the solid.

Answer

Sometimes equilibria for complex ions are described in terms of dissociation constants, K_d. For the complex ion AlF3−6AlF63− the dissociation reaction is:

AlF3−6⇌Al3++6F−\)and$Kd=[Al3+][F−]6[AlF3−6]=2\times10−24(15.E.33)(15.E.33)AlF63−\rightleftharpoons Al3++6F−$and\(Kd=[Al3+][F−]6[AlF63−]=2×10−24

63. Calculate the value of the formation constant, K_f, for AlF3−6AlF63−.

Answer

5×10^{23}

64. Using the value of the formation constant for the complex ion Co(NH3)2+6Co(NH3)62+, calculate the dissociation constant.

65. Using the dissociation constant, $K_d = 7.8 \times 10^{-18}$, calculate the equilibrium concentrations of Cd^{2+} and CN^- in a 0.250-M solution of Cd(CN)2−4Cd(CN)42−.

Answer

This table has two main columns and three rows. The first row for the first column does not have a heading and then has the following in the first column: Initial concentration (M) and Equilibrium (M). The second column has the header, “[C d (C N) subscript 4 to the second power superscript negative sign] [C N superscript negative sign] [C d to the second power superscript positive sign].” Under the second column is a subgroup of two rows and three columns. The first column contains the following: 0.250 and 0.250 minus x. The second column contains the following: 0 and 4 x. The third column contains the following: 0 and x.

$[Cd^{2+}] = 9.5 \times 10^{-5}$ *M*; $[CN^{-}] = 3.8 \times 10^{-4}$ *M*

66. Using the dissociation constant, $K_d = 3.4 \times 10^{-15}$, calculate the equilibrium concentrations of Zn^{2+} and OH^{-} in a 0.0465-*M* solution of Zn(OH)2−4Zn(OH)42−.

67. Using the dissociation constant, $K_d = 2.2 \times 10^{-34}$, calculate the equilibrium concentrations of Co^{3+} and NH_3 in a 0.500-*M* solution of Co(NH3)3+6Co(NH3)63+.

Answer

$[Co^{3+}] = 3.0 \times 10^{-6}$ *M*; $[NH_3] = 1.8 \times 10^{-5}$ *M*

68. Using the dissociation constant, $K_d = 1 \times 10^{-44}$, calculate the equilibrium concentrations of Fe^{3+} and CN^{-} in a 0.333 M solution of Fe(CN)3−6Fe(CN)63−.

69. Calculate the mass of potassium cyanide ion that must be added to 100 mL of solution to dissolve 2.0×10^{-2} mol of silver cyanide, AgCN.

Answer

1.3 g

70. Calculate the minimum concentration of ammonia needed in 1.0 L of solution to dissolve 3.0×10^{-3} mol of silver bromide.

71. A roll of 35-mm black and white photographic film contains about 0.27 g of unexposed AgBr before developing. What mass of $Na_2S_2O_3$•$5H_2O$ (sodium thiosulfate pentahydrate or hypo) in 1.0 L of developer is required to dissolve the AgBr as Ag(S2O3)3−2Ag(S2O3)23− ($K_f = 4.7 \times 10^{13}$)?

Answer

0.80 g

72. We have seen an introductory definition of an acid: An acid is a compound that reacts with water and increases the amount of hydronium ion present. In the chapter on acids and bases, we saw two more definitions of acids: a compound that donates a proton (a hydrogen ion, H^{+}) to another compound is called a Brønsted-Lowry acid, and a Lewis acid is any species that can accept a pair of electrons. Explain why the introductory definition is a macroscopic definition, while the Brønsted-Lowry definition and the Lewis definition are microscopic definitions.

73. Write the Lewis structures of the reactants and product of each of the following equations, and identify the Lewis acid and the Lewis base in each:

a. CO2+OH−⟶HCO3−

b. B(OH)3+OH−⟶B(OH)4−

c. I−+I2⟶I3−

d. AlCl3+Cl−⟶AlCl4− (use Al-Cl single bonds)

e. O2−+SO3⟶SO42−

Answer

(a)

This figure shows a chemical reaction modeled with structural formulas. On the left side is a structure with a central C atom. O atoms, each with two unshared electron pairs, are double bonded to the left and right sides of the C atom. Following a plus sign is another structure in brackets which has an O atom with three unshared electron dot pairs single bonded to an H atom on the right. Outside the brackets is superscript negative sign. Following a right pointing arrow is a structure in brackets that has a central C atom to which 3 O atoms are bonded. Above and slightly to the right, one of the O atoms is connected with a double bond. This O atom has two unshared electron pairs. The second O atom is single bonded below and slightly to the right. This O atom has three unshared electron pairs. The third O atom is bonded to the left of the C atom. This O atom has two unshared electron pairs and an H atom single bonded to its left. Outside the brackets to the right is a superscript negative symbol.

;

(b)

This figure shows a chemical reaction modeled with structural formulas. On the left side is a structure that has a central B atom to which 3 O atoms are bonded. The O atoms above and below slightly right of the B atom each have an H atom single bonded to the right. The third O atom is single bonded to the left side of the B atom. This O atom has an H atom single bonded to its left side. All O atoms in this structure have two unshared electron pairs. Following a plus sign is another structure which has an O atom single bonded to an H atom on its right. The O atom has three unshared electron pairs. The structure appears in brackets with a superscript negative sign. Following a right pointing arrow is a structure in brackets has a central B atom to which 4 O atoms are bonded. The O atoms above, below, and right of the B atom each hav an H atom single bonded to the right. The third O atom is single bonded to the left side of the B atom. This O atom has an H atom single bonded to its left side. All O atoms in this structure have two unshared electron pairs. Outside the brackets to the right is a superscript negative symbol.

;

(c)

This figure illustrates a chemical reaction using structural formulas. On the left, two I atoms, each with 3 unshared electron pairs, are joined with a single bond. Following a plus sign is another structure which has an I atom with four pairs of electron dots and a superscript negative sign. Following a right pointing arrow is a structure in brackets that has three I atoms connected in a line with single bonds. The two end I atoms have three unshared electron dot pairs and the I atom at the center has two unshared electron pairs. Outside the brackets is a superscript negative sign.

;

(d)

This figure illustrates a chemical reaction using structural formulas. On the left, an A l atom is positioned at the center of a structure and three Cl atoms are single bonded above, leftt, and below. Each C l atom has three pairs of electron dots. Following a plus sign is another structure which has an F atom is surrounded by four electron dot pairs and a superscript negative symbol. Following a right pointing arrow is a structure in brackets that has a central A l atom to which 4 C l atoms are connected with single bonds above, below, to the left, and to the right. Each C l atom in this structure has three pairs of electron dots. Outside the brackets is a superscript negative symbol.

;

(e)

This figure illustrates a chemical reaction using structural formulas. On the left is a structure which has an S atom at the center. O atoms are single bonded above and below. These O atoms have three electron dot pairs each. To the right of the S atom is a double bonded O atom which has two pairs of electron dots. Following a plus sign is an O atom which is surrounded by four electron dot pairs and has a superscript 2 negative. Following a right pointing arrow is a structure in brackets that has a central S atom to which 4 O atoms are connected with single bonds above, below, to the left, and to the right. Each of the O atoms has three pairs of electron dots. Outside the brackets is a superscript 2 negative.

74. Write the Lewis structures of the reactants and product of each of the following equations, and identify the Lewis acid and the Lewis base in each:

1. $CS2+SH−\longrightarrow HCS3−$
2. $BF3+F−\longrightarrow BF4−$
3. $I−+SnI2\longrightarrow SnI3−$
4. $Al(OH)3+OH−\longrightarrow Al(OH)4−$
5. $F−+SO3\longrightarrow SFO3−$

75. Using Lewis structures, write balanced equations for the following reactions:

a. $HCl(g)+PH3(g)\longrightarrow HCl(g)+PH3(g)$

b. $H3O++CH−3\longrightarrow H3O++CH3$

c. $CaO+SO3\longrightarrow CaO+SO3\longrightarrow$

d. $NH+4+C2H5O−\longrightarrow NH4++C2H5O$

Answer

(a)

This figure represents a chemical reaction in two rows. The top row shows the reaction using chemical formulas. The second row uses structural formulas to represent the reaction. The first row contains the equation H C l (g) plus P H subscript 3 (g) right pointing arrow left bracket P H subscript 4 right bracket superscript plus plus left bracket C l with 4 pairs of electron dots right bracket superscript negative sign. The second row begins on the left with H left bracket C l with four unshared electron pairs right bracket plus a structure in brackets with a central P atom with H atoms single bonded at the left, above, and to the right. A single unshared electron pair is on the central P atom. Outside the brackets to the right is a superscript plus sign. Following a right pointing arrow is a structure in brackets with a central P atom with H atoms single bonded at the left, above, below, and to the right. Outside the brackets is a superscript plus sign. This structure is followed by a plus and a C l atom in brackets with four unshared electron pairs and a superscript negative sign.

;

(b) $H3O++CH−3\longrightarrow CH4+H2OH3O++CH3−\longrightarrow CH4+H2O$

This figure represents a chemical reaction using structural formulas. A structure is shown in brackets on the left which is composed of a central O atom with one unshared electron pair and three single bonded H atoms to the left, right, and above the atom. Outside the brackets to the right is a superscript plus sign. Following a plus sign, is another structure in brackets composed of a central C atom with one unshared electron pair and three single bonded H atoms to the left, right, and above the atom. Outside the brackets to the right is a superscript negative sign. Following a right pointing arrow is a structure with a central C atom with H atoms single bonded above, below, left and right. Following a plus sign is a structure with a central O atom with two unshared electron pairs and two H atoms connected with single bonds.

;

(c) $CaO+SO3\longrightarrow CaSO4CaO+SO3\longrightarrow CaSO4$

This figure represents a chemical reaction using structural formulas. On the left, C a superscript 2 plus is just left of bracket O with four unshared electron pairs right bracket superscript 2 negative plus a structure with a central S atom to which two O atoms are single bonded at the left and right, and a single O atom is double bonded above. The two single bonded O atoms each have three unshared electron pairs and the double bonded O atom has two unshared electron pairs. Following a right pointing arrow is C a superscript 2 plus just left of a structure in brackets with a central S atom which has 4 O atoms single bonded at the left, above, below, and to the right. Each of the O atoms has three unshared electron pairs. Outside the brackets to the right is a superscript two negative.

;

(d) NH+4+C2H5O−⟶C2H5OH+NH3NH4++C2H5O−⟶C2H5OH+NH3

This figure represents a chemical reaction using structural formulas. A structure is shown in brackets on the left which is composed of a central N atom with four single bonded H atoms to the left, right, above, and below the atom. Outside the brackets to the right is a superscript plus sign. Following a plus sign, is another structure in brackets composed of a C atom with three single bonded H atoms above, below, and to the left. A second C atom is single bonded to the right. This C atom has H atoms single bonded above and below. To the right of the second C atom, an O atom is single bonded. This O atom has three unshared electron pairs. Outside the brackets to the right is a subperscript negative. Following a right pointing arrow is a structure composed of a C atom with three single bonded H atoms above, below, and to the left. A second C atom is single bonded to the right. This C atom has H atoms single bonded above and below. To the right of the second C atom, an O atom is single bonded. This O atom has two unshared electron pairs and an H atom single bonded to its right.

76. Calculate [HgCl42−] in a solution prepared by adding 0.0200 mol of NaCl to 0.250 L of a 0.100-*M* $HgCl_2$ solution.

77. In a titration of cyanide ion, 28.72 mL of 0.0100 *M* $AgNO_3$ is added before precipitation begins. [The reaction of Ag^+ with $CN^–$ goes to completion, producing the Ag(CN)2− complex.] Precipitation of solid AgCN takes place when excess Ag^+ is added to the solution, above the amount needed to complete the formation of Ag(CN)2−. How many grams of NaCN were in the original sample?

Answer

0.0281 g

78. What are the concentrations of Ag^+, $CN^–$, and Ag(CN)−2Ag(CN)2− in a saturated solution of AgCN?

79. In dilute aqueous solution HF acts as a weak acid. However, pure liquid HF (boiling point = 19.5 °C) is a strong acid. In liquid HF, HNO_3 acts like a base and accepts protons. The acidity of liquid HF can be increased by adding one of several inorganic fluorides that are Lewis acids and accept $F^–$ ion (for example, BF_3 or SbF_5). Write balanced chemical equations for the reaction of pure HNO_3 with pure HF and of pure HF with BF_3.

Answer

HNO3(l)+HF(l)⟶H2NO+3+F−HNO3(l)+HF(l)⟶H2NO3++F−; HF(l)+BF3(g)⟶H++BF4HF(l)+BF3(g)⟶H++BF4

80. The simplest amino acid is glycine, $H_2NCH_2CO_2H$. The common feature of amino acids is that they contain the functional groups: an amine group, $–NH_2$, and a carboxylic acid group, $–CO_2H$. An amino acid can function as either an acid or a base. For glycine, the acid strength of the carboxyl group is about the same as that of acetic acid, CH_3CO_2H, and the base strength of the amino group is slightly greater than that of ammonia, NH_3.

81. Write the Lewis structures of the ions that form when glycine is dissolved in 1 *M* HCl and in 1 *M* KOH.

82. Write the Lewis structure of glycine when this amino acid is dissolved in water. (Hint: Consider the relative base strengths of the $–NH_2$ and −CO−2−CO2− groups.)

83. Boric acid, H_3BO_3, is not a Brønsted-Lowry acid but a Lewis acid.

1. Write an equation for its reaction with water.
2. Predict the shape of the anion thus formed.
3. What is the hybridization on the boron consistent with the shape you have predicted?

Answer

H3BO3+H2O⟶H4BO−4+H+H3BO3+H2O⟶H4BO4−+H+; The electronic and molecular shapes are the same—both tetrahedral. The tetrahedral structure is consistent with sp^3 hybridization.

7.9.3: Multiple Equilibria

84. A saturated solution of a slightly soluble electrolyte in contact with some of the solid electrolyte is said to be a system in equilibrium. Explain. Why is such a system called a heterogeneous equilibrium?

85. Calculate the equilibrium concentration of Ni^{2+} in a 1.0-*M* solution $[Ni(NH_3)_6](NO_3)_2$.

Answer

0.014 *M*

86. Calculate the equilibrium concentration of Zn^{2+} in a 0.30-*M* solution of Zn(CN)42−.

87. Calculate the equilibrium concentration of Cu^{2+} in a solution initially with 0.050 *M* Cu^{2+} and 1.00 *M* NH_3.

Answer

1.0×10^{-13} *M*

88. Calculate the equilibrium concentration of Zn^{2+} in a solution initially with 0.150 *M* Zn^{2+} and 2.50 *M* CN^{-}.

89. Calculate the Fe^{3+} equilibrium concentration when 0.0888 mole of $K_3[Fe(CN)_6]$ is added to a solution with 0.0.00010 *M* CN^{-}.

Answer

9×10^{-22} *M*

90. Calculate the Co^{2+} equilibrium concentration when 0.100 mole of $[Co(NH_3)_6](NO_3)_2$ is added to a solution with 0.025 *M* NH_3. Assume the volume is 1.00 L.

91. The equilibrium constant for the reaction Hg2+(aq)+2Cl−(aq)⇌HgCl2(aq)Hg2+(aq)+2Cl−(aq)⇌HgCl2(aq) is 1.6×10^{13}. Is $HgCl_2$ a strong electrolyte or a weak electrolyte? What are the concentrations of Hg^{2+} and Cl^{-} in a 0.015-*M* solution of $HgCl_2$?

Answer

6.2×10^{-6} *M* = $[Hg^{2+}]$; 1.2×10^{-5} *M* = $[Cl^{-}]$; The substance is a weak electrolyte because very little of the initial 0.015 *M* $HgCl_2$ dissolved.

92. Calculate the molar solubility of $Sn(OH)_2$ in a buffer solution containing equal concentrations of NH_3 and NH4+.

93. Calculate the molar solubility of $Al(OH)_3$ in a buffer solution with 0.100 *M* NH_3 and 0.400 *M* NH4+.

Answer

$[OH^{-}] = 4.5 \times 10^{-5}$; $[Al^{3+}] = 2.1 \times 10^{-20}$ (molar solubility)

94. What is the molar solubility of CaF_2 in a 0.100-*M* solution of HF? K_a for HF = 7.2×10^{-4}.

95. What is the molar solubility of $BaSO_4$ in a 0.250-*M* solution of $NaHSO_4$? K_a for HSO4− = 1.2×10^{-2}.

Answer

[SO42−]=0.049M; $[Ba^{2+}] = 2.2 \times 10^{-9}$ (molar solubility)

96. What is the molar solubility of $Tl(OH)_3$ in a 0.10-*M* solution of NH_3?

97. What is the molar solubility of $Pb(OH)_2$ in a 0.138-*M* solution of CH_3NH_2?

Answer

$[OH^{-}] = 7.6 \times 10^{-3}$ *M*, $[Pb^{2+}] = 4.8 \times 10^{-12}$ (molar solubility)

98. A solution of 0.075 *M* $CoBr_2$ is saturated with H_2S ($[H_2S]$ = 0.10 *M*). What is the minimum pH at which CoS begins to precipitate?

CoS(s)⇌Co2+(aq)+S2−(aq)Ksp=4.5×10−27CoS(s)⇌Co2+(aq)+S2−(aq)Ksp=4.5×10−27

H2S(aq)+2H2O(l)⇌2H3O+(aq)+S2−(aq)K=1.0×10−26H2S(aq)+2H2O(l)⇌2H3O+(aq)+S2−(aq)K=1.0×10−26

99. A 0.125-*M* solution of $Mn(NO_3)_2$ is saturated with H_2S ($[H_2S]$ = 0.10 *M*). At what pH does MnS begin to precipitate?

MnS(s)⇌Mn2+(aq)+S2−(aq)Ksp=4.3×10−22MnS(s)⇌Mn2+(aq)+S2−(aq)Ksp=4.3×10−22

H2S(aq)+2H2O(l)⇌2H3O+(aq)+S2−(aq)K=1.0×10−26H2S(aq)+2H2O(l)⇌2H3O+(aq)+S2−(aq)K=1.0×10−26

Answer

3.27

100. Calculate the molar solubility of BaF_2 in a buffer solution containing 0.20 *M* HF and 0.20 *M* NaF.

101. Calculate the molar solubility of $CdCO_3$ in a buffer solution containing 0.115 *M* Na_2CO_3 and 0.120 *M* $NaHCO_3$

Answer

[CO32−]=0.115M; $[Cd^{2+}] = 3 \times 10^{-12}$ *M*

102. To a 0.10-M solution of $Pb(NO_3)_2$ is added enough $HF(g)$ to make [HF] = 0.10 M.

1. Does PbF_2 precipitate from this solution? Show the calculations that support your conclusion.
2. What is the minimum pH at which PbF_2 precipitates?

Calculate the concentration of Cd^{2+} resulting from the dissolution of $CdCO_3$ in a solution that is 0.010 M in H_2CO_3.

Answer

1×10^{-5} M

103. Both AgCl and AgI dissolve in NH_3.

1. What mass of AgI dissolves in 1.0 L of 1.0 M NH_3?
2. What mass of AgCl dissolves in 1.0 L of 1.0 M NH_3?

104. Calculate the volume of 1.50 M CH_3CO_2H required to dissolve a precipitate composed of 350 mg each of $CaCO_3$, $SrCO_3$, and $BaCO_3$.

Answer

0.0102 L (10.2 mL)

105. Even though $Ca(OH)_2$ is an inexpensive base, its limited solubility restricts its use. What is the pH of a saturated solution of $Ca(OH)_2$?

106. What mass of NaCN must be added to 1 L of 0.010 M $Mg(NO_3)_2$ in order to produce the first trace of $Mg(OH)_2$?

Answer

5×10^{-3} g

107. Magnesium hydroxide and magnesium citrate function as mild laxatives when they reach the small intestine. Why do magnesium hydroxide and magnesium citrate, two very different substances, have the same effect in your small intestine. (Hint: The contents of the small intestine are basic.)

108. The following question is taken from a Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

Solve the following problem:

$MgF2(s) \rightleftharpoons Mg^{2+}(aq) + 2F-(aq)$

In a saturated solution of MgF_2 at 18 °C, the concentration of Mg^{2+} is 1.21×10^{-3} M. The equilibrium is represented by the preceding equation.

1. Write the expression for the solubility-product constant, K_{sp}, and calculate its value at 18 °C.
2. Calculate the equilibrium concentration of Mg^{2+} in 1.000 L of saturated MgF_2 solution at 18 °C to which 0.100 mol of solid KF has been added. The KF dissolves completely. Assume the volume change is negligible.
3. Predict whether a precipitate of MgF_2 will form when 100.0 mL of a 3.00×10^{-3}-M solution of $Mg(NO_3)_2$ is mixed with 200.0 mL of a 2.00×10^{-3}-M solution of NaF at 18 °C. Show the calculations to support your prediction.
4. At 27 °C the concentration of Mg^{2+} in a saturated solution of MgF_2 is 1.17×10^{-3} M. Is the dissolving of MgF_2 in water an endothermic or an exothermic process? Give an explanation to support your conclusion.

Answer

$K_{sp} = [Mg^{2+}][F^-]^2 = (1.21 \times 10^{-3})(2 \times 1.21 \times 10^{-3})^2 = 7.09 \times 10^{-9}$; 7.09×10^{-7} M

Determine the concentration of Mg^{2+} and F^- that will be present in the final volume. Compare the value of the ion product $[Mg^{2+}][F^-]^2$ with K_{sp}. If this value is larger than K_{sp}, precipitation will occur. $0.1000\text{ L} \times 3.00 \times 10^{-3}$ M $Mg(NO_3)_2$ = 0.3000 L × M $Mg(NO_3)_2$ M $Mg(NO_3)_2$ = 1.00×10^{-3} M 0.2000 L × 2.00×10^{-3} M NaF = 0.3000 L × M NaF M NaF = 1.33×10^{-3} M ion product = $(1.00 \times 10^{-3})(1.33 \times 10^{-3})^2 = 1.77 \times 10^{-9}$ This value is smaller than K_{sp}, so no precipitation will occur. MgF_2 is less soluble at 27 °C than at 18 °C. Because added heat acts like an added reagent, when it appears on the product side, the Le Chatelier's principle states that the equilibrium will shift to the reactants' side to counter the stress. Consequently, less reagent will dissolve. This situation is found in our case. Therefore, the reaction is exothermic.

109. Which of the following compounds, when dissolved in a 0.01-*M* solution of $HClO_4$, has a solubility greater than in pure water: CuCl, $CaCO_3$, MnS, $PbBr_2$, CaF_2? Explain your answer.

110. Which of the following compounds, when dissolved in a 0.01-*M* solution of $HClO_4$, has a solubility greater than in pure water: AgBr, BaF_2, $Ca_3(PO_4)_3$, ZnS, PbI_2? Explain your answer.

Answer

BaF_2, $Ca_3(PO_4)_2$, ZnS; each is a salt of a weak acid, and the [H3O+][H3O+] from perchloric acid reduces the equilibrium concentration of the anion, thereby increasing the concentration of the cations

111. What is the effect on the amount of solid $Mg(OH)_2$ that dissolves and the concentrations of Mg^{2+} and OH^- when each of the following are added to a mixture of solid $Mg(OH)_2$ and water at equilibrium?

1. $MgCl_2$
2. KOH
3. $HClO_4$
4. $NaNO_3$
5. $Mg(OH)_2$

112. What is the effect on the amount of $CaHPO_4$ that dissolves and the concentrations of Ca^{2+} and HPO−4HPO4− when each of the following are added to a mixture of solid $CaHPO_4$ and water at equilibrium?

- $CaCl_2$
- HCl
- $KClO_4$
- NaOH
- $CaHPO_4$

Answer

Effect on amount of solid $CaHPO_4$, $[Ca^{2+}]$, $[OH^-]$: increase, increase, decrease; decrease, increase, decrease; no effect, no effect, no effect; decrease, increase, decrease; increase, no effect, no effect

113. Identify all chemical species present in an aqueous solution of $Ca_3(PO_4)_2$ and list these species in decreasing order of their concentrations. (Hint: Remember that the PO43− ion is a weak base.

114. A volume of 50 mL of 1.8 *M* NH_3 is mixed with an equal volume of a solution containing 0.95 g of $MgCl_2$. What mass of NH_4Cl must be added to the resulting solution to prevent the precipitation of $Mg(OH)_2$?

Answer

7.1 g

CHAPTER OVERVIEW

8: Thermodynamics

8.1: Spontaneity- The Meaning of Spontaneous Change

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 $8.1.1$).

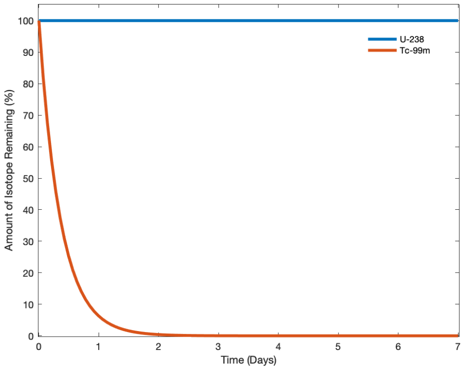


Figure $8.1.1$: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts)

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 $8.1.2$).

$$\mathrm{C(s, diamond)} \longrightarrow \mathrm{C(s, graphite)} \tag{8.1.1}$$

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.

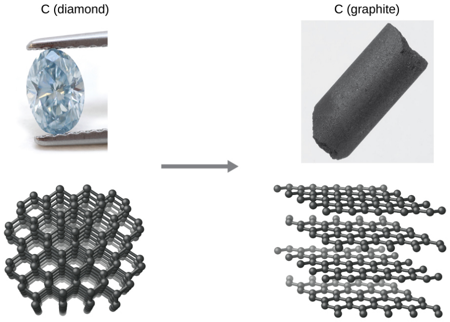


Figure $8.1.2$: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at temperatures 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 $8.1.3$). 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.

$$w = -P\Delta V \tag{8.1.2}$$

$$= 0 \quad (\mathrm{P = 0 \text{ in a vaccum}}) \tag{8.1.3}$$

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.

$$\Delta U = q + w \quad \text{(First Law of Thermodynamics)}$$
$$= 0 + 0 = 0 \tag{8.1.4}$$

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).

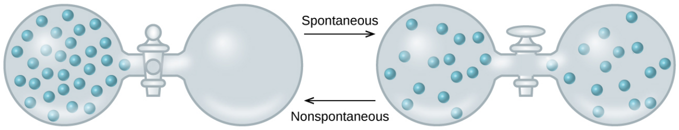


Figure 8.1.3: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

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 8.1.4). 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.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0 \tag{8.1.5}$$

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 8.1.4: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 8.1.1: 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

Figure 8.1.5:(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 8.1.1

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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8.2: The Concept of Entropy

Learning Objectives

- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

The first law of thermodynamics governs changes in the state function we have called internal energy (U). 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.

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 8.2.1.

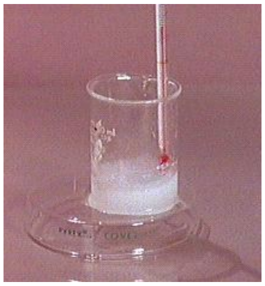


Figure 8.2.1: An Endothermic Reaction. The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic, so water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes 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 https://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. In Chapter 13, we introduced the concept of entropy in relation to solution formation. Here we further explore the nature of this state function and define it mathematically.

Entropy and Microstates

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure 8.2.2) published the results of an extensive study regarding the efficiency of steam heat engines. In a later review of Carnot's findings, Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). The term reversible process refers to a process that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change is some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.

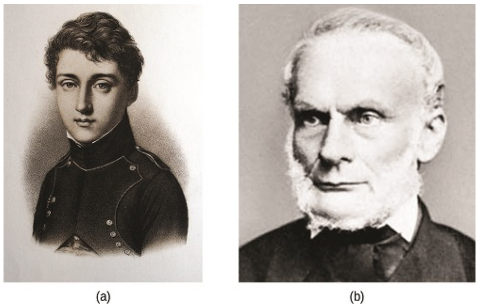


Figure 8.2.2: (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, and so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property entropy (S) and defined its change for any process as the following:

$$\Delta S = \frac{q_{\mathrm{rev}}}{T} \tag{8.2.1}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

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 (W) is a specific configuration of the locations and energies of the atoms or molecules that comprise a system like the following:

$$S = k \ln W \tag{8.2.2}$$

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:

$$\Delta S = S_{\mathrm{f}} - S_{\mathrm{i}} = k \ln W_{\mathrm{f}} - k \ln W_{\mathrm{i}} = k \ln \frac{W_{\mathrm{f}}}{W_{\mathrm{i}}} \tag{8.2.3}$$

For processes involving an increase in the number of microstates, $W_f > W_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $W_f < W_i$, 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 8.2.3. 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, *the most probable distribution is therefore the one of greatest entropy*.

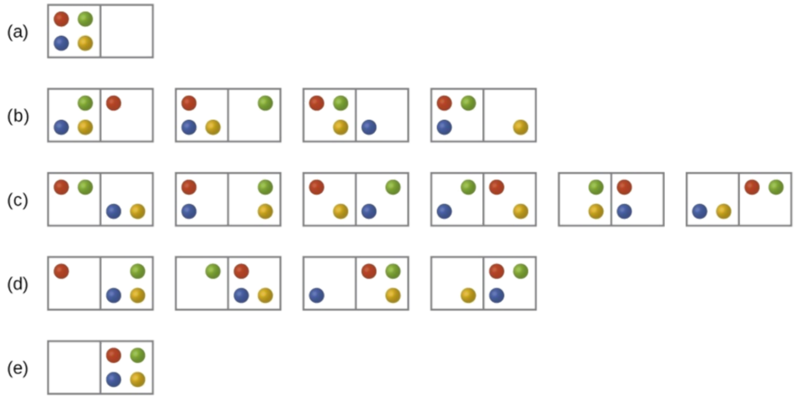


Figure 8.2.3: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

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

$$\frac{6}{16}\backslash)or\backslash(\frac{3}{8} \tag{8.2.4}$$

The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (d), each with a probability of

$$\frac{1}{16} \tag{8.2.5}$$

The probability of finding all particles in only one box (either the left box or right box) is then

$$\left(\frac{1}{16}+\frac{1}{16}\right)=\frac{2}{16}\backslash)or\backslash(\frac{1}{8} \tag{8.2.6}$$

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.

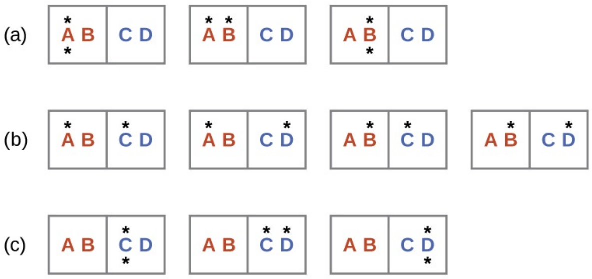
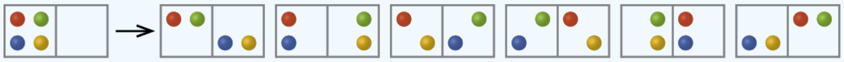


Figure 8.2.4: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow 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 8.2.4. 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.

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:

$$\Delta S = k \ln \frac{W_\text{c}}{W_\text{a}} = 1.38 \times 10^{-23}\ \text{J/K} \times \ln \frac{6}{1} = 2.47 \times 10^{-23}\ \text{J/K} \tag{8.2.7}$$

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 8.2.1

Consider the system shown in Figure 8.2.3. 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

Entropy: https://youtu.be/dkanY87VsjY

Predicting the Sign of ΔS

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 $8.2.5$. 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, $S_{\text{liquid}} > S_{\text{solid}}$ 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, $\Delta S < 0$.

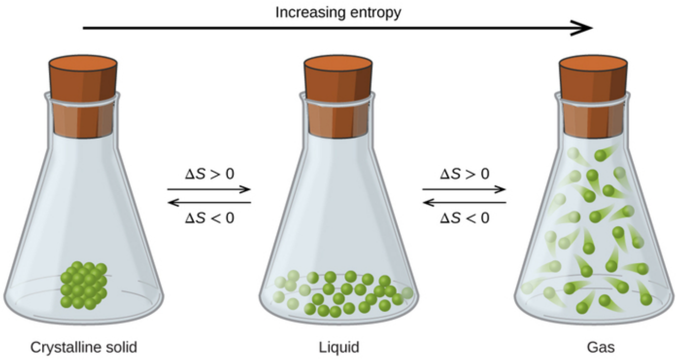


Figure $8.2.5$: The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

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, $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$, 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 $8.2.6$).

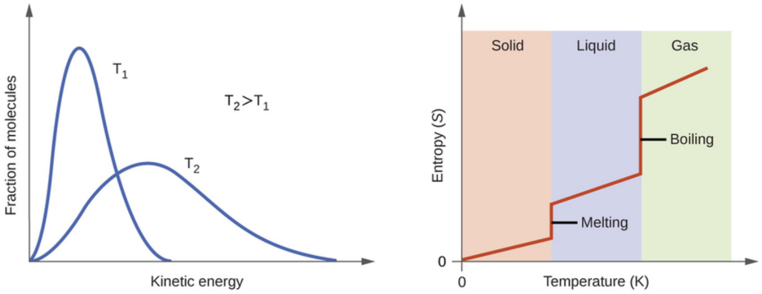


Figure $8.2.6$: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

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 affects 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 .

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 8.2.2

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. (b) Negative; The liquid becomes a more ordered solid. (c) Positive; The relatively ordered solid becomes a gas. (d) Positive; There is a net production of one mole of gas.

Note

Entropy (S) is a thermodynamic property of all substances. The greater the number of possible microstates for a system, the greater the disorder and the higher the 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 8.2.4, 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 $\mathrm{Na^+}$ ion becomes hydrated by an ordered arrangement of at least six water molecules, and the $\mathrm{Cl^-}$ 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 $\Delta S_{soln} > 0$.

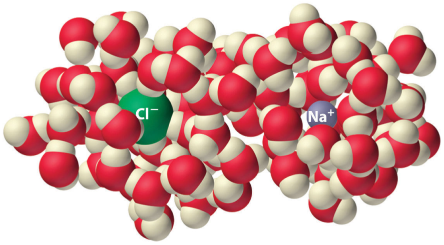


Figure 8.2.7 The Effect of Solution Formation on Entropy

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 8.2.3

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 8.2.3

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)
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

Reversible and Irreversible Changes

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, $\Delta U = q + w$. Because U is a state function, the magnitude of ΔU does not depend on reversibility and is independent of the path taken. So

$$\Delta U = q_{rev} + w_{rev} = q_{irrev} + w_{irrev} \tag{8.2.8}$$

Note

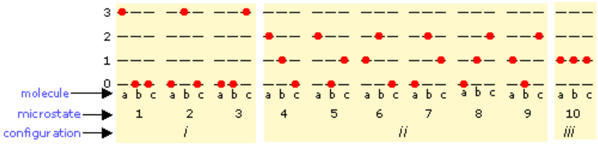
Work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$.

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.

Quantum states and Energy Spreading

At the atomic and molecular level, all energy is *quantized*; each particle possesses discrete states of kinetic energy and is able to accept thermal energy only in packets whose values correspond to the energies of one or more of these states. Polyatomic molecules can store energy in rotational and vibrational motions, and all molecules (even monatomic ones) will possess translational kinetic energy (thermal energy) at all temperatures above absolute zero. The energy difference between adjacent translational states is so minute that translational kinetic energy can be regarded as *continuous* (non-quantized) for most practical purposes.

The number of ways in which thermal energy can be distributed amongst the allowed states within a collection of molecules is easily calculated from simple statistics, but we will confine ourselves to an example here. Suppose that we have a system consisting of three molecules and three quanta of energy to share among them. We can give all the kinetic energy to any one molecule, leaving the others with none, we can give two units to one molecule and one unit to another, or we can share out the energy equally and give one unit to each molecule. All told, there are ten possible ways of distributing three units of energy among three identical molecules as shown here:



Each of these ten possibilities represents a distinct *microstate* that will describe the system at any instant in time. Those microstates that possess identical distributions of energy among the accessible quantum levels (and differ only in which particular molecules occupy the levels) are known as **configurations**. Because all microstates are equally probable, the probability of any one configuration is proportional to the number of microstates that can produce it. Thus in the system shown above, the configuration labeled *ii* will be observed 60% of the time, while *iii* will occur only 10% of the time.

As the number of molecules and the number of quanta increases, the number of accessible microstates grows explosively; if 1000 quanta of energy are shared by 1000 molecules, the number of available microstates will be around 10^{600}— a number that greatly exceeds the number of atoms in the observable universe! The number of possible configurations (as defined above) also increases, but in such a way as to greatly reduce the probability of all but the most probable configurations. Thus for a sample of a gas large enough to be observable under normal conditions, only a single configuration (energy distribution amongst the quantum states) need be considered; even the second-most-probable configuration can be neglected.

The bottom line: any collection of molecules large enough in numbers to have chemical significance will have its therrmal energy distributed over an unimaginably large number of microstates. The number of microstates increases exponentially as more energy states ("configurations" as defined above) become accessible owing to

- Addition of energy quanta (higher temperature),
- Increase in the number of molecules (resulting from dissociation, for example).
- the volume of the system increases (which decreases the spacing between energy states, allowing more of them to be populated at a given temperature.)

Key Concepts and Summary

- For a given system, the greater the number of microstates, the higher the entropy.
- During a spontaneous process, the entropy of the universe increases.

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{8.2.9}$$

Entropy (S) is a state function whose value increases with an increase in the number of available microstates. 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. Entropy (*S*) 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, $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$ 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.

Key Equations

- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $S = k \ln W$
- $\Delta S = k \ln \frac{W_{\text{f}}}{W_{\text{i}}}$

Glossary

entropy (*S*)

state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates often described as a measure of the disorder of the system

microstate (*W*)

possible configuration or arrangement of matter and energy within a system

reversible process

process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes removed

Contributors and Attributions

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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).

8.3: Evaluating Entropy and Entropy Changes

Learning Objectives

- To use thermodynamic cycles to calculate changes in entropy.

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 8.3.1). 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 effects). Such a state of perfect order (or, conversely, zero disorder) corresponds to zero entropy. 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.

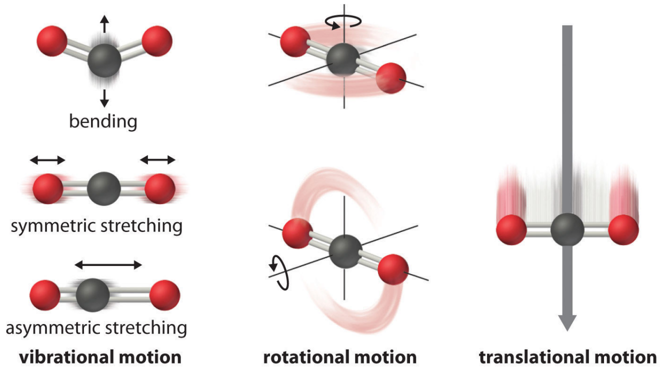


Figure 8.3.1: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion and have zero entropy. In practice, this is an unattainable ideal.

Third Law of Thermodynamics

The entropy of any perfectly ordered, crystalline substance at absolute zero 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 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. 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.

Calculating ΔS from Standard Molar Entropy Values

One way of calculating ΔS for a reaction is to use tabulated values of the standard molar entropy (S°), which is the entropy of 1 mol of a substance at a standard temperature of 298 K; the units of S° 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 J/(mol•K)] and 298 K.

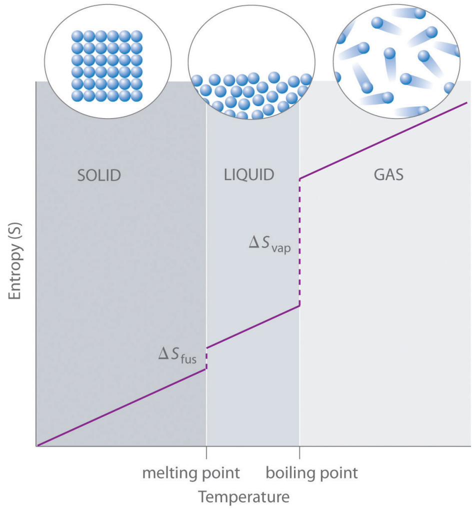


Figure 8.3.2: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (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}).

As shown in Table 8.3.1, for substances with approximately the same molar mass and number of atoms, S° values fall in the order S°(gas) > S°(liquid) > S°(solid). For instance, S° for liquid water is 70.0 J/(mol•K), whereas S° for water vapor is 188.8 J/(mol•K). Likewise, S° is 260.7 J/(mol•K) for gaseous I_2 and 116.1 J/(mol•K) for solid I2. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases. The correlation between physical state and absolute entropy is illustrated in Figure 8.3.2, which is a generalized plot of the entropy of a substance versus temperature.

Table 8.3.1: Standard Molar Entropy Values of Selected Substances at 25°C

Gases		**Liquids**		**Solids**	
Substance	*S° [J/(mol•K)]*	*Substance*	*S° [J/(mol•K)]*	*Substance*	*S° [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

Note

Entropy increases with softer, less rigid solids, solids that contain larger atoms, and solids with complex molecular structures.

A closer examination of Table 8.3.1 also reveals that substances with similar molecular structures tend to have similar S° 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° = 2.4 J/(mol•K)]. In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher S° [5.7 J/(mol•K)] due to more disorder 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° values for $CH_3OH(l)$ and $CH_3CH_2OH(l)$. Finally, substances with strong hydrogen bonds have lower values of S°, which reflects a more ordered structure.

Note

ΔS° for a reaction can be calculated from absolute entropy values using the same "products minus reactants" rule used to calculate ΔH°.

To calculate ΔS° 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 8.3.1 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

✓ Example 8.3.1

Use the data in Table 8.3.1 to calculate ΔS° 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 8.3.1. 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° for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

$$\mathrm{C_8H_{18}(l)} + \frac{25}{2}\mathrm{O_2(g)} \rightarrow 8\mathrm{CO_2(g)} + 9\mathrm{H_2O(g)}$$

We calculate ΔS° for the reaction using the "products minus reactants" rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$\begin{align}
\Delta S^\circ_{\text{rxn}} &= \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants}) \tag{8.3.1}\\
&= [8S^\circ(\mathrm{CO_2}) + 9S^\circ(\mathrm{H_2O})] - [S^\circ(\mathrm{C_8H_{18}}) + \frac{25}{2}S^\circ(\mathrm{O_2})] \tag{8.3.2}\\
&= \{[8\text{ mol CO}_2 \times 213.8\text{ J}/(\text{mol}\cdot\text{K})] + [9\text{ mol H}_2\text{O} \times 188.8\text{ J}/(\text{mol}\cdot\text{K})]\} \tag{8.3.3}\\
&- \left\{[1\text{ mol C}_8\text{H}_{18} \times 329.3\text{ J}/(\text{mol}\cdot\text{K})] + \left[\frac{25}{2}\text{ mol O}_2 \times 205.2\text{ J}/(\text{mol}\cdot\text{K})\right]\right\} \tag{8.3.4}\\
&= 515.3\text{ J/K} \tag{8.3.5}
\end{align}$$

ΔS° is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

? Exercise 8.3.1

Use the data in Table 8.3.1 to calculate ΔS° for the reaction of $H_2(g)$ with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}).

Answer: −361.1 J/K

Calculating ΔS from Thermodynamic Cycles

We can also calculate a change in entropy using a thermodynamic cycle. As you learned previously, the molar heat capacity (C_p) is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant pressure. Similarly, C_v is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant volume. The increase in entropy with increasing temperature in Figure 8.3.2 is approximately proportional to the heat capacity of the substance.

Recall that the entropy change (ΔS) is related to heat flow (q_{rev}) by $\Delta S = q_{rev}/T$. Because $q_{rev} = nC_p\Delta T$ at constant pressure or $nC_v\Delta T$ at constant volume, where n is the number of moles of substance present, the change in entropy for a substance whose temperature changes from T_1 to T_2 is as follows:

$$\Delta S = \frac{q_{\text{rev}}}{T} = nC_{\text{p}}\frac{\Delta T}{T} \quad \text{(constant pressure)} \tag{8.3.6}$$

As you will discover in more advanced math courses than is required here, it can be shown that this is equal to the following:For a review of natural logarithms, see Essential Skills 6 in Chapter 11.

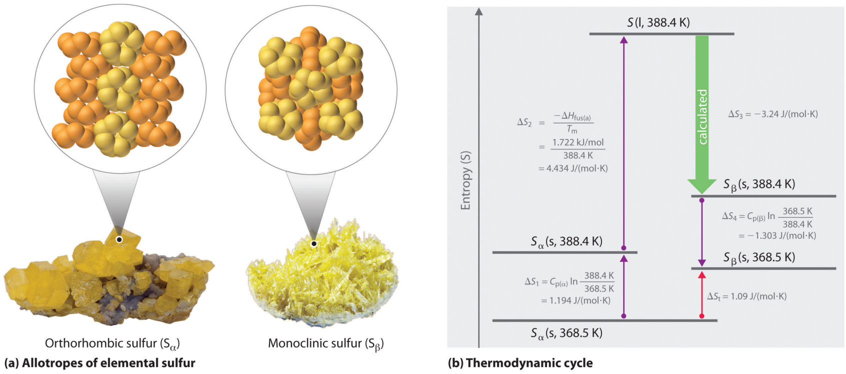
$$\Delta S = nC_{\text{p}} \ln\frac{T_2}{T_1} \quad \text{(constant pressure)} \tag{8.3.7}$$

Similarly,

$$\Delta S = nC_{\text{v}} \ln\frac{T_2}{T_1} \quad \text{(constant volume)} \tag{8.3.8}$$

Thus we can use a combination of heat capacity measurements (Equation 18.20 or Equation 18.21) and experimentally measured values of enthalpies of fusion or vaporization if a phase change is involved (Equation 18.18) to calculate the entropy change corresponding to a change in the temperature of a sample.

We can use a thermodynamic cycle to calculate the entropy change when the phase change for a substance such as sulfur cannot be measured directly. As noted in the exercise in Example 6, elemental sulfur exists in two forms (part (a) in Figure 8.3.3): an orthorhombic form with a highly ordered structure (S_α) and a less-ordered monoclinic form (S_β). The orthorhombic (α) form is more stable at room temperature but undergoes a phase transition to the monoclinic (β) form at temperatures greater than 95.3°C (368.5 K). The transition from S_α to S_β can be described by the thermodynamic cycle shown in part (b) in Figure 8.3.3, in which liquid sulfur is an intermediate. The change in entropy that accompanies the conversion of liquid sulfur to S_β ($-\Delta S_{fus(\beta)} = \Delta S_3$ in the cycle) cannot be measured directly. Because entropy is a state function, however, ΔS_3 can be calculated from the overall entropy change (ΔS_t) for the S_α–S_β transition, which equals the sum of the ΔS values for the steps in the thermodynamic cycle, using Equation 18.20 and tabulated thermodynamic parameters (the heat capacities of S_α and S_β, $\Delta H_{fus(\alpha)}$, and the melting point of S_α.)



(a) Allotropes of elemental sulfur

(b) Thermodynamic cycle

Figure 8.3.3: Two Forms of Elemental Sulfur and a Thermodynamic Cycle Showing the Transition from One to the Other(a) Orthorhombic sulfur (S_α) has a highly ordered structure in which the S_8 rings are stacked in a “crankshaft” arrangement. Monoclinic sulfur (S_β) is also composed of S_8 rings but has a less-ordered structure. (b) At 368.5 K, S_α undergoes a phase transition to S_β. Although ΔS_3 cannot be measured directly, it can be calculated using the values shown in this thermodynamic cycle.

If we know the melting point of S_α (T_m = 115.2°C = 388.4 K) and ΔS_t for the overall phase transition [calculated to be 1.09 J/(mol•K) in the exercise in Example 6], we can calculate ΔS_3 from the values given in part (b) in Figure 8.3.3 where $C_{p(\alpha)}$ = 22.70 J/mol•K and $C_{p(\beta)}$ = 24.77 J/mol•K (subscripts on ΔS refer to steps in the cycle):

$$\Delta S_{\mathrm{t}} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 \tag{8.3.9}$$

$$1.09\ \mathrm{J/(mol\cdot K)} = C_{\mathrm{p}(\alpha)} \ln\left(\frac{T_2}{T_1}\right) + \frac{\Delta H_{\mathrm{fus}}}{T_{\mathrm{m}}} + \Delta S_3 + C_{\mathrm{p}(\beta)} \ln\left(\frac{T_4}{T_3}\right) \tag{8.3.10}$$

$$= 22.70\ \mathrm{J/(mol\cdot K)} \ln\left(\frac{388.4}{368.5}\right) + \left(\frac{1.722\ \mathrm{kJ/mol}}{388.4\ \mathrm{K}} \times 1000\ \mathrm{J/kJ}\right) \tag{8.3.11}$$

$$+ \Delta S_3 + 24.77\ \mathrm{J/(mol\cdot K)} \ln\left(\frac{368.5}{388.4}\right) \tag{8.3.12}$$

$$= [1.194\ \mathrm{J/(mol\cdot K)}] + [4.434\ \mathrm{J/(mol\cdot K)}] + \Delta S_3 + [-1.303\ \mathrm{J/(mol\cdot K)}] \tag{8.3.13}$$

Solving for ΔS_3 gives a value of −3.24 J/(mol•K). As expected for the conversion of a less ordered state (a liquid) to a more ordered one (a crystal), ΔS_3 is negative.

How are Entropies Measured

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 melting, for example, is just $\Delta H_{fusion}/T_m$.
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 dT/T* for each increment of temperature dT. This is of course just the integral

$$S_{0 \rightarrow T^o} = \int_0^{T^o} \frac{C_p}{T} dt \tag{8.3.14}$$

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 above integral in place of a constant *C*.

$$S_{0 \rightarrow T^o} = \int_0^{T^o} \frac{C_p(T)}{T} dt \tag{8.3.15}$$

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.

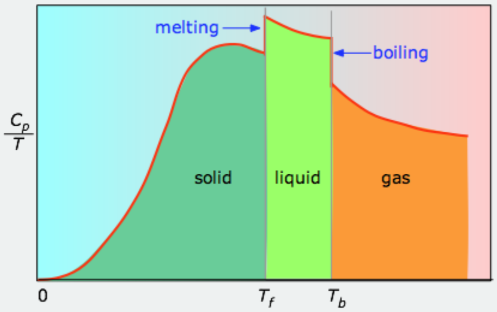


Figure 8.3.4: Heat capitity/temperature as a function of temperature

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. Values of C_p for temperatures near zero are not measured directly, but can be estimated from quantum theory.

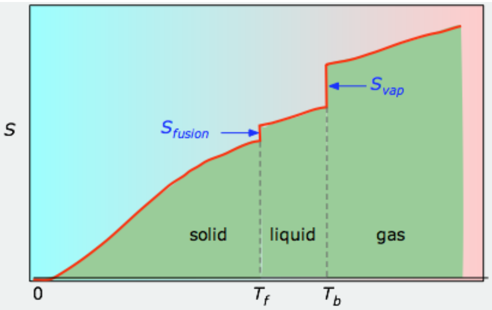


Figure 8.3.5: Molar entropy as a function of temperature

The cumulative areas from 0 K to any given temperature (taken from the experimental plot on the left) are then plotted as a function of *T*, and any phase-change entropies such as $S_{vap} = H_{vap} / T_b$ are added to obtain the absolute entropy at temperature *T*.

Summary

- Entropy changes can be calculated using the “products minus reactants” rule or from a combination of heat capacity measurements and measured values of enthalpies of fusion or vaporization.

The third law of thermodynamics states that the entropy of any perfectly ordered, crystalline substance at absolute zero is zero. At temperatures greater than absolute zero, entropy has a positive value, which allows us to measure the absolute entropy of a substance. Measurements of the heat capacity of a substance and the enthalpies of fusion or vaporization can be used to calculate the changes in entropy that accompany a physical change. The entropy of 1 mol of a substance at a standard temperature of 298 K is its standard molar entropy (S°). We can use the “products minus reactants” rule to calculate the standard entropy change (ΔS°) for a reaction using tabulated values of S° for the reactants and the products.

8.4: Criteria for Spontaneous Change- The Second Law of Thermodynamics

Learning Objectives

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

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* ($\Delta S > 0$) 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:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{8.4.1}$$

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:

   $$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}} \tag{8.4.2}$$

   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:

   $$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}} \tag{8.4.3}$$

   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, $T_{\text{sys}} \approx T_{\text{surr}}$, 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 8.4.1.

Table 8.4.1: The Second Law of Thermodynamics

$\Delta S_{\text{univ}} > 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{\text{univ}} = 0$	reversible (system is at equilibrium)

Definition: The Second Law of Thermodynamics

All spontaneous changes cause an increase in the entropy of the universe.

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:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \tag{8.4.4}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example 8.4.1.

✓ Will Ice Spontaneously Melt?

The entropy change for the process

$$\mathrm{H_2O}(s) \longrightarrow \mathrm{H_2O}(l)$$

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:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\ \text{J/K} + \frac{-6.00 \times 10^3\ \text{J}}{263.15\ \text{K}} = -0.7\ \text{J/K}\end{aligned}$$

$S_{\text{univ}} < 0$, so melting is nonspontaneous (*not* spontaneous) at −10.0 °C.

At 10.00 °C (283.15 K), the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$$

$$= 22.1\ \text{J/K} + \frac{-6.00 \times 10^3\ \text{J}}{283.15\ \text{K}} = +0.9\ \text{J/K}$$

$S_{\text{univ}} > 0$, so melting *is* spontaneous at 10.00 °C.

? Exercise 8.4.1

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{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.

Gibbs Energy and Changes of Gibbs Energy

One of the challenges of using the second law of thermodynamics to determine if a process is spontaneous is that we must determine the entropy change for the system *and* the entropy change for the surroundings. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the Gibbs free energy change (G) (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS \tag{8.4.5}$$

Free energy is a state function, and at constant temperature and pressure, the standard free energy change (ΔG°) may be expressed as the following:

$$\Delta G = \Delta H - T\Delta S \tag{8.4.6}$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.) We can understand the relationship between this system property and the spontaneity of a process by recalling the previously derived second law expression:

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T} \tag{8.4.7}$$

The first law requires that qsurr = −qsys, and at constant pressure qsys = ΔH, and so this expression may be rewritten as the following:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T} \tag{8.4.8}$$

ΔH is the enthalpy change of the system. Multiplying both sides of this equation by −T, and rearranging yields the following:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S \tag{8.4.9}$$

Comparing this equation to the previous one for free energy change shows the following relation:

$$\Delta G = -T\Delta S_{\text{univ}} \tag{8.4.10}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ}. Table 8.4.2 expands on Table 8.4.2 and summarizes the relation between the spontaneity of a process and the arithmetic signs of ΔG and ΔS indicators.

Table 8.4.2: Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{\text{univ}} > 0$	$\Delta G < 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	$\Delta G > 0$	nonspontaneous
$\Delta S_{\text{univ}} = 0$	$\Delta G = 0$	reversible (at equilibrium)

. Willard Gibbs (1839–1903)

Born in Connecticut, Josiah Willard Gibbs attended Yale, as did his father, a professor of sacred literature at Yale, who was involved in the Amistad trial. In 1863, Gibbs was awarded the first engineering doctorate granted in the United States. He was appointed professor of mathematical physics at Yale in 1871, the first such professorship in the United States. His series of papers entitled "On the Equilibrium of Heterogeneous Substances" was the foundation of the field of physical chemistry and is considered one of the great achievements of the 19th century. Gibbs, whose work was translated into French by Le Chatelier, lived with his sister and brother-in-law until his death in 1903, shortly before the inauguration of the Nobel Prizes.

Gibbs energy is a state function, so its value depends only on the conditions of the initial and final states of the system that have undergone some change. A convenient and common approach to the calculation of free energy changes for physical and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute standard free energy changes according to the following relation as demonstrated in Example 8.4.1.

ΔG°=ΔH°−TΔS° \label{\(\PageIndex{7}\)}

The Definition of Gibbs Free Energy: https://youtu.be/iuWkcHUh-1o

Example 8.4.2: Evaluation of ΔG°

Change from ΔH° and ΔS° Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for ΔG° say about the spontaneity of this process?

Solution

The process of interest is the following:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$$

The standard change in free energy may be calculated using the following equation:

$$\Delta G^\circ_{298} = \Delta H^\circ - T\Delta S^\circ$$

From Appendix G, here is the data:

Substance	$\Delta H^\circ_\mathrm{f}$ (kJ/mol)	S°_{298} (J/K·mol)
$\mathrm{H_2O}(l)$	−286.83	70.0
$\mathrm{H_2O}(g)$	−241.82	188.8

Combining at 298 K:

$$\Delta H^\circ = \Delta H^\circ_{298} = \Delta H^\circ_\mathrm{f}(\mathrm{H_2O}(g)) - \Delta H^\circ_\mathrm{f}(\mathrm{H_2O}(l))$$
$$= [-241.82\ \mathrm{kJ} - (-285.83)]\ \mathrm{kJ/mol} = 44.01\ \mathrm{kJ/mol}$$

$$\Delta S^\circ = \Delta S^\circ_{298} = S^\circ_{298}(\mathrm{H_2O}(g)) - S^\circ_{298}(\mathrm{H_2O}(l))$$
$$= 188.8\ \mathrm{J/mol\cdot K} - 70.0\ \mathrm{J/K} = 118.8\ \mathrm{J/mol\cdot K}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Converting everything into kJ and combining at 298 K:

$$\Delta G^\circ_{298} = \Delta H^\circ - T\Delta S^\circ$$

$$= 44.01\ \mathrm{kJ/mol} - (298\ \mathrm{K} \times 118.8\ \mathrm{J/mol\cdot K}) \times \frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}}$$

$$44.01\ \mathrm{kJ/mol} - 35.4\ \mathrm{kJ/mol} = 8.6\ \mathrm{kJ/mol}$$

At 298 K (25 °C) $\Delta G^\circ_{298} > 0$, and so boiling is nonspontaneous (not spontaneous).

? Exercise 8.4.2

Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for ΔG° say about the spontaneity of this process?

$$C_2H_6(g) \longrightarrow H_2(g) + C_2H_4(g)$$

Answer:

$\Delta G^\circ_{298} = 102.0\ \text{kJ/mol}$; the reaction is nonspontaneous (not spontaneous) at 25 °C.

Free energy changes may also use the standard free energy of formation $(\Delta G^\circ_\text{f})$, for each of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpies of formation, $(\Delta G^\circ_\text{f})$ is by definition zero for elemental substances under standard state conditions. The approach to computing the free energy change for a reaction using this approach is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction

$$m\text{A} + n\text{B} \longrightarrow x\text{C} + y\text{D}, \tag{8.4.11}$$

the standard free energy change at room temperature may be calculated as

$$\Delta G^\circ_{298} = \Delta G^\circ = \sum \nu \Delta G^\circ_{298}(\text{products}) - \sum \nu \Delta G^\circ_{298}(\text{reactants}) \tag{8.4.12}$$

$$= [x\Delta G^\circ_\text{f}(\text{C}) + y\Delta G^\circ_\text{f}(\text{D})] - [m\Delta G^\circ_\text{f}(\text{A}) + n\Delta G^\circ_\text{f}(\text{B})]. \tag{8.4.13}$$

✓ Example 8.4.3: Calculation of ΔG°_{298}

Consider the decomposition of yellow mercury(II) oxide.

$$\text{HgO}(s,\ \text{yellow}) \longrightarrow \text{Hg}(l) + \frac{1}{2}\text{O}_2(g)$$

Calculate the standard free energy change at room temperature, ΔG°_{298}, using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous under standard conditions?

Solution

The required data are available in Appendix G and are shown here.

Compound	ΔG°_f (kJ/mol)	ΔH°_f (kJ/mol)	S°_{298} (J/K·mol)
HgO (*s*, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
$O_2(g)$	0	0	205.2

(a) Using free energies of formation:

$$\Delta G^\circ_{298} = \sum \nu G S^\circ_{298}(\text{products}) - \sum \nu \Delta G^\circ_{298}(\text{reactants})$$

$$= \left[1\Delta G^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta G^\circ_{298}\text{O}_2(g)\right] - 1\Delta G^\circ_{298}\text{HgO}(s,\ \text{yellow})$$

$$= \left[1\ \text{mol}(0\ \text{kJ/mol}) + \frac{1}{2}\text{mol}(0\ \text{kJ/mol})\right] - 1\ \text{mol}(-58.43\ \text{kJ/mol}) = 58.43\ \text{kJ/mol}$$

(b) Using enthalpies and entropies of formation:

$$\Delta H^\circ_{298} = \sum \nu \Delta H^\circ_{298}(\text{products}) - \sum \nu \Delta H^\circ_{298}(\text{reactants})$$

$$= \left[1 \Delta H^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta H^\circ_{298}\text{O}_2(g)\right] - 1 \Delta H^\circ_{298}\text{HgO}(s,\ \text{yellow})$$

$$= [1\ \text{mol}(0\ \text{kJ/mol}) + \frac{1}{2}\text{mol}(0\ \text{kJ/mol})] - 1\ \text{mol}(-90.46\ \text{kJ/mol}) = 90.46\ \text{kJ/mol}$$

$$\Delta S^\circ_{298} = \sum \nu \Delta S^\circ_{298}(\text{products}) - \sum \nu \Delta S^\circ_{298}(\text{reactants})$$

$$= \left[1 \Delta S^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta S^\circ_{298}\text{O}_2(g)\right] - 1 \Delta S^\circ_{298}\text{HgO}(s,\ \text{yellow})$$

$$= \left[1\ \text{mol}(75.9\ \text{J/mol K}) + \frac{1}{2}\text{mol}(205.2\ \text{J/mol K})\right] - 1\ \text{mol}(71.13\ \text{J/mol K}) = 107.4\ \text{J/mol K}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 90.46\ \text{kJ} - 298.15\ \text{K} \times 107.4\ \text{J/K} \cdot \text{mol} \times \frac{1\ \text{kJ}}{1000\ \text{J}}$$

$$\Delta G^\circ = (90.46 - 32.01)\ \text{kJ/mol} = 58.45\ \text{kJ/mol}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is nonspontaneous (not spontaneous) at room temperature.

? Exercise 8.4.3

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (Appendix G). Do the results indicate the reaction to be spontaneous or nonspontaneous at 25 °C?

$$\text{C}_2\text{H}_4(g) \longrightarrow \text{H}_2(g) + \text{C}_2\text{H}_2(g)$$

Answer

−141.5 kJ/mol, nonspontaneous

Key Concepts and Summary

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. Gibbs free energy (G) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A negative value for ΔG indicates a spontaneous process; a positive ΔG indicates a nonspontaneous process; and a ΔG of zero indicates that the system is at equilibrium. A number of approaches to the computation of free energy changes are possible.

Key Equations

- $\Delta S^\circ = \Delta S^\circ_{298} = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants})$
- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$
- $\Delta G = \Delta H - T\Delta S$
- $\Delta G = \Delta G^\circ + RT \ln Q$
- $\Delta G^\circ = -RT \ln K$

Glossary

Gibbs free energy change (G)

thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in G

standard free energy change ($\Delta G°$)

change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

standard free energy of formation $(\Delta G_{\mathrm{f}}^{\circ})$

change in free energy accompanying the formation of one mole of substance from its elements in their standard states

second law of thermodynamics

entropy of the universe increases for a spontaneous process

standard entropy ($S°$)

entropy for a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K and denoted S_{298}°

standard entropy change ($\Delta S°$)

change in entropy for a reaction calculated using the standard entropies, usually at room temperature and denoted ΔS_{298}°

Contributors and Attributions

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8.5: Standard Gibbs Energy Change, ΔG°

Learning Objectives

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate free energy change for a process using free energies of formation for its reactants and products
- Calculate free energy change for a process using enthalpies of formation and the entropies for its reactants and products

The Gibbs free energy (G), often called simply free energy, was named in honor of J. Willard Gibbs (1838–1903), an American physicist who first developed the concept. It is defined in terms of three other state functions with which you are already familiar: enthalpy, temperature, and entropy:

$$G = H - TS \tag{8.5.1}$$

Because it is a combination of state functions, G is also a state function.

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,

$$\Delta G = \Delta H - T\Delta S \tag{8.5.2}$$

where all thermodynamic quantities are those of the *system*. Under standad conditions Equation 8.5.2 is then expressed at

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{8.5.3}$$

Since G is a state function, ΔG^o can be obtained from the *standard free-energy of formation* values in Table T1 (or T2) via the similar relationship used to calculate other state functions like ΔH^o and ΔS^o:

$$\Delta G^o = \sum n\Delta G_f^o\,(products) - \sum m\Delta G_f^o\,(reactants) \tag{8.5.4}$$

Example 8.5.1: Calculation of ΔG°_{298}

Consider the decomposition of yellow mercury(II) oxide.

$$\mathrm{HgO}(s,\ \text{yellow}) \longrightarrow \mathrm{Hg}(l) + \frac{1}{2}\mathrm{O_2}(g)$$

Calculate the standard free energy change at room temperature, ΔG°_{298}, using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous under standard conditions? The required data are available in Table T1 .

Solution

The required data are available in Table T1 and are shown here.

Compound	$\Delta G^\circ_\mathrm{f}$ (kJ/mol)	$\Delta H^\circ_\mathrm{f}$ (kJ/mol)	S°_{298} (J/K·mol)
HgO (*s*, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
$O_2(g)$	0	0	205.2

(a) Using free energies of formation:

$$\Delta G^\circ_{298} = \sum \nu GS^\circ_{298}(\text{products}) - \sum \nu\Delta G^\circ_{298}(\text{reactants})$$

$$= \left[1\Delta G^\circ_{298}\mathrm{Hg}(l) + \frac{1}{2}\Delta G^\circ_{298}\mathrm{O_2}(g)\right] - 1\Delta G^\circ_{298}\mathrm{HgO}(s,\ \text{yellow})$$

$$= \left[1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})\right] - 1\text{ mol}(-58.43\text{ kJ/mol}) = 58.43\text{ kJ/mol}$$

(b) Using enthalpies and entropies of formation:

$$\Delta H^\circ_{298} = \sum \nu \Delta H^\circ_{298}(\text{products}) - \sum \nu \Delta H^\circ_{298}(\text{reactants})$$

$$= \left[1\Delta H^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta H^\circ_{298}\text{O}_2(g)\right] - 1\Delta H^\circ_{298}\text{HgO}(s,\text{ yellow})$$

$$= [1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})] - 1\text{ mol}(-90.46\text{ kJ/mol}) = 90.46\text{ kJ/mol}$$

$$\Delta S^\circ_{298} = \sum \nu \Delta S^\circ_{298}(\text{products}) - \sum \nu \Delta S^\circ_{298}(\text{reactants})$$

$$= \left[1\Delta S^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta S^\circ_{298}\text{O}_2(g)\right] - 1\Delta S^\circ_{298}\text{HgO}(s,\text{ yellow})$$

$$= \left[1\text{ mol}(75.9\text{ J/mol K}) + \frac{1}{2}\text{mol}(205.2\text{ J/mol K})\right] - 1\text{ mol}(71.13\text{ J/mol K}) = 107.4\text{ J/mol K}$$

Now use these values in Equation 8.5.3 to get ΔG^o:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 90.46\text{ kJ} - 298.15\text{ K} \times 107.4\text{ J/K}\cdot\text{mol} \times \frac{1\text{ kJ}}{1000\text{ J}}$$

$$\Delta G^\circ = (90.46 - 32.01)\text{ kJ/mol} = 58.45\text{ kJ/mol}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is nonspontaneous (not spontaneous) at room temperature (since $\Delta G^o > 0$.

? Exercise 8.5.1

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (Appendix G). Do the results indicate the reaction to be spontaneous or nonspontaneous at 25 °C?

$$C_2H_4(g) \longrightarrow H_2(g) + C_2H_2(g)$$

Answer

−141.5 kJ/mol, nonspontaneous

Calculating Gibbs Free Energy (Grxn) for a Reaction: https://youtu.be/wmreE6zeFQo

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8.6: Gibbs Energy Change and Equilibrium

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.
- The sign of the standard free energy change $\Delta G°$ of a chemical reaction determines whether the reaction will tend to proceed in the forward or reverse direction.
- Similarly, the relative signs of $\Delta G°$ and $\Delta S°$ determine whether the spontaniety of a chemical reaction will be affected by the temperature, and if so, in what way.

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.

Temperature Dependence to ΔG

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).

$$H_2O_{(l)} \rightarrow H_2O_{(s)} \tag{8.6.1}$$

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.

Note

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:

- ΔG < 0: reaction can spontaneously proceed to the right:

$$A \rightarrow B \tag{8.6.2}$$

- ΔG > 0: reaction can spontaneously proceed to the left:

$$A \leftarrow B \tag{8.6.3}$$

- ΔG = 0: the reaction is at equilibrium; the quantities of [A] and [B] will not change

Recall the condition for spontaneous change

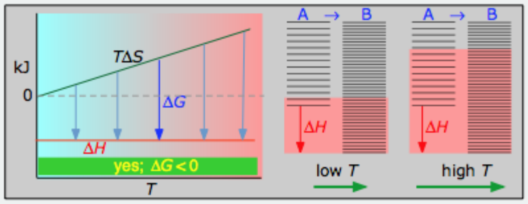
$$\Delta G = \Delta H - T\Delta S < 0 \tag{8.6.4}$$

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.

The following cases generalizes these relations for the four sign-combinations of Δ*H* and Δ*S*. (Note that use of the standard Δ*H*° and Δ*S*° values in the example reactions is not strictly correct here, and can yield misleading results when used generally.)

> 0

Under these conditions, both the Δ*H* and *T*Δ*S* terms will be negative, so Δ*G* will be negative regardless of the temperature. An exothermic reaction whose entropy increases will be spontaneous at all temperatures.



Example Reaction

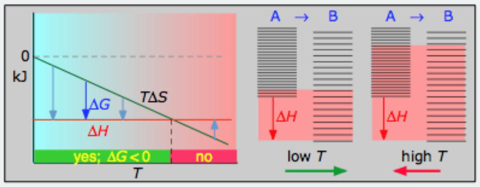
$$C_{(graphite)} + O_{2(g)} \rightleftharpoons CO_{2(g)} \tag{8.6.5}$$

- Δ*H*° = –393 kJ
- Δ*S*° = +2.9 J K^{-1}
- Δ*G*° = –394 kJ at 298 K

The positive entropy change is due mainly to the greater mass of CO_2 molecules compared to those of O_2.

< 0

If the reaction is sufficiently exothermic it can force Δ*G* negative only at temperatures below which |*T*Δ*S*| < |Δ*H*|. This means that there is a temperature *T* = Δ*H* / Δ*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.



Example reaction:

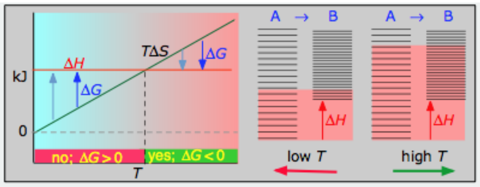
$$3H_2 + N_2 \rightleftharpoons 2NH_{3(g)} \tag{8.6.6}$$

- ΔH° = –46.2 kJ
- ΔS° = –389 J K–1
- ΔG° = –16.4 kJ at 298 K

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.

> 0

This is the reverse of the previous case; the entropy increase must overcome the handicap of an endothermic process so that TΔS > ΔH. Since the effect of the temperature is to "magnify" the influence of a positive ΔS, the process will be spontaneous at temperatures above T = ΔH / ΔS. (Think of melting and boiling.)



Example reaction:

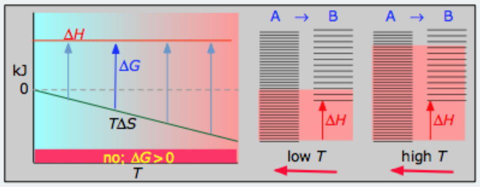
$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \tag{8.6.7}$$

- Δ*H*° = 55.3 kJ
- Δ*S*° = +176 J K^{-1}
- Δ*G*° = +2.8 kJ at 298 K

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.

< 0

With both Δ*H and* Δ*S* 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.



Example reaction:

$$½N_2 + O_2 \rightleftharpoons NO_{2(g)} \tag{8.6.8}$$

- Δ*H*° = 33.2 kJ
- ΔS° = –249 J K^{-}1
- Δ*G*° = +51.3 kJ at 298 K

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.

The above cases and associated plots 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 Δ*H* and Δ*S*.

- Their most important differentiating features are the position of the Δ*H* line (above or below the is *T*Δ*S* line), and the slope of the latter, which of course depends on the sign of Δ*S*.
- The reaction A → B will occur spontaneously only when Δ*G* is negative (blue arrows pointing down.)
- Owing to the slight temperature dependence of Δ*S*, the *T*Δ*S* plots are not quite straight lines as shown here. Similarly, the lines representing Δ*H* 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 Δ*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 Δ*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!

Liquid-Vapor Equilibrium

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. If this process 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, we know that for 1 mol of water,

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} = \frac{40{,}657\ \text{J}}{373.15\ \text{K}} = 108.96\ \text{J/K}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\Delta G_{100^\circ\text{C}} = \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} = 40{,}657\ \text{J} - [(373.15\ \text{K})(108.96\ \text{J/K})] = 0\ \text{J} \tag{8.6.9}$$

The energy required for vaporization offsets the increase in disorder of the system. Thus ΔG = 0, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

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

$$\Delta G_{110^\circ\text{C}} = \Delta H - T\Delta S = 40{,}657\ \text{J} - [(383.15\ \text{K})(108.96\ \text{J/K})] = -1091\ \text{J} \tag{8.6.10}$$

At 110°C, ΔG < 0, and vaporization is predicted to occur spontaneously and irreversibly.

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:

$$\Delta G_{90^\circ\text{C}} = \Delta H - T\Delta S = 40{,}657\ \text{J} - [(363.15\ \text{K})(108.96\ \text{J/K})] = 1088\ \text{J} \tag{8.6.11}$$

At 90°C, ΔG > 0, and water does not spontaneously convert to water vapor. 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.

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 8.6.4), setting ΔG = 0, and solving for T,

$$0\ \text{J} = 40{,}657\ \text{J} - T(108.96\ \text{J/K})$$
$$T = 373.15\ \text{K}$$

Thus ΔG = 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 8.6.1 shows how the ΔH and TΔS terms vary with temperature for the vaporization of water. When the two lines cross, ΔG = 0, and ΔH = TΔS.

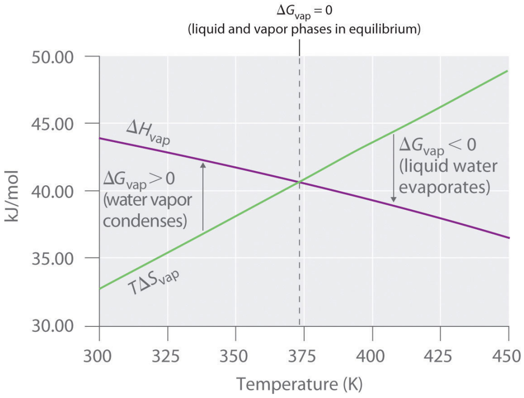


Figure 8.6.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH − TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the TΔS term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than TΔS, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid.

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 (ΔH > 0), which converts the albumin to a highly disordered structure in which the molecules aggregate as a disorganized solid (ΔS > 0). At temperatures greater than 373 K, the TΔS term dominates, and ΔG < 0, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.

Free Energy and the Equilibrium Constant

Δ*G* is key 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 Δ*G*. It is far more convenient to work with the equilibrium constant of a reaction, within which Δ*G* is "hidden". This is just as well, because for most reactions (those that take place in solutions or gas mixtures) the value of Δ*G* 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 Δ*H*.

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. 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):

$$\Delta G = V\Delta P - S\Delta T \tag{8.6.12}$$

If a reaction is carried out at constant temperature (ΔT = 0), then Equation 8.6.12 simplifies to

$$\Delta G = V\Delta P \tag{8.6.13}$$

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 8.6.13 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):

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P = nRT\frac{\Delta P}{P} = nRT\ln\left(\frac{P_\mathrm{f}}{P_\mathrm{i}}\right) \tag{8.6.14}$$

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:

$$G - G^\circ = nRT\ln P \tag{8.6.15}$$

This can be rearranged as follows:

$$G = G^{\circ} + nRT\ln P \tag{8.6.16}$$

As you will soon discover, Equation 8.6.16 allows us to relate ΔG° 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:

$$aA + bB \rightleftharpoons cC + dD \tag{8.6.17}$$

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:

$$\delta G = \sum_m G_{products} - \sum_n G_{reactants} = (cG_C + dG_D) - (aG_A + bG_B) \tag{8.6.18}$$

Substituting Equation 8.6.16 for each term into Equation 8.6.18,

$$\Delta G = [(cG^o_C + cRT\ln P_C) + (dG^o_D + dRT\ln P_D)] - [(aG^o_A + aRT\ln P_A) + (bG^o_B + bRT\ln P_B)] \tag{8.6.19}$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^{\circ} + RT\ln\left(\frac{P^c_{\mathrm{C}}P^d_{\mathrm{D}}}{P^a_{\mathrm{A}}P^b_{\mathrm{B}}}\right) = \Delta G^{\circ} + RT\ln Q \tag{8.6.20}$$

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, ΔG = 0 for a system at equilibrium. Therefore, we can describe the relationship between ΔG° and K_p for gases as follows:

$$0 = \Delta G^{\circ} + RT\ln K_p \tag{8.6.21}$$

$$\Delta G^{\circ} = -RT\ln K_p \tag{8.6.22}$$

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.

Note

For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.

✓ Example 8.6.1

We previosuly calculated that ΔG° = −32.7 kJ/mol of N_2 for the reaction

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

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:

- $P_{\mathrm{N_2}}$ = 2.00 atm,
- $P_{\mathrm{H_2}}$ = 7.00 atm,
- $P_{\mathrm{NH_3}}$ = 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 8.6.20, calculate Q.

B. Substitute the values of ΔG° and Q into Equation 8.6.20 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG° and ΔG under nonstandard conditions is given in Equation 8.6.20. Substituting the partial pressures given, we can calculate Q:

$$Q = \frac{P^2_{\mathrm{NH_3}}}{P_{\mathrm{N_2}} P^3_{\mathrm{H_2}}} = \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7}$$

B Substituting the values of ΔG° and Q into Equation 8.6.20,

$$\begin{aligned} \Delta G = \Delta G^\circ + RT \ln Q &= -32.7 \text{ kJ} + \left[(8.314 \text{ J/K})(373 \text{ K})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)\ln(6.4 \times 10^{-7})\right] \\ &= -32.7 \text{ kJ} + (-44 \text{ kJ}) \\ &= -77 \text{ kJ/mol of } \mathrm{N_2} \end{aligned}$$

Because ΔG < 0 and Q < 1.0, the reaction is spontaneous to the right as written, so products are favored over reactants.

? Exercise 8.6.1

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, $P_{\mathrm{O_2}}$ = 0.200 atm, and $P_{\mathrm{NO_2}}$ = 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 8.6.2

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C. As calculated in Example 10, ΔG° for this reaction is −32.7 kJ/mol of N_2.

Given: balanced chemical equation from Example 10, ΔG°, and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG° and T (in kelvins) into Equation ??? to 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 8.6.22,

$$\begin{aligned} \Delta G^\circ &= -RT \ln K_\mathrm{p} \\ \frac{-\Delta G^\circ}{RT} &= \ln K_\mathrm{p} \end{aligned}$$

Inserting the value of ΔG° and the temperature (25°C = 298 K) into this equation,

$$\begin{aligned} \ln K_\mathrm{p} &= -\frac{(-32.7 \text{ kJ})(1000 \text{ J/kJ})}{(8.314 \text{ J/K})(298 \text{ K})} = 13.2 \\ K_\mathrm{p} &= 5.4 \times 10^5 \end{aligned}$$

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 8.6.2

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. As calculated in the exercise in Example 10, 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 in Chapter 15 and showed that they are related:

$$K_p = K(RT)^{\Delta n} \tag{8.6.23}$$

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, Δn = 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 8.6.22 can be written in a more general form:

$$\Delta G^{\circ} = -RT\ln K \tag{8.6.24}$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 8.6.24 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 8.6.24 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:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = -RT\ln K \tag{8.6.25}$$

Equation 8.6.25 is quite powerful and connected the nature of the system under equilibrium K to the condition of the system under standard conditions ΔG^o.; that is quite powerful. 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.

Note

The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum entropy and seek the lowest energy state possible.

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 8.6.2). 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.

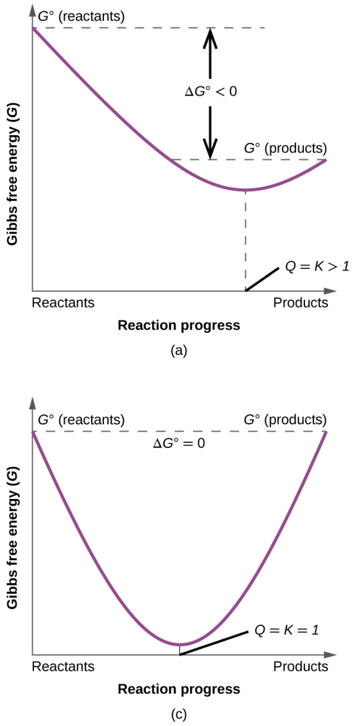


Figure 8.6.2: These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium.

Relating Grxn and Kp: https://youtu.be/T-OYNTYN__4

ΔG° and ΔG: Predicting the Direction of Chemical 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 8.6.26:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8.6.26}$$

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG° depends on the relative magnitudes of the ΔH° and TΔS° terms. It is important to recognize that a positive value of ΔG° 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.

Note

A positive ΔG° means that the equilibrium constant is less than 1.

Example 8.6.3

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 8.6.26, the calculated value of ΔS°, and other data given to calculate ΔG° for the reaction. Use the value of ΔG° to determine whether the reaction is spontaneous as written.

Solution

A To calculate ΔG° 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:

$$\begin{aligned} \Delta S^\circ &= S^\circ(\mathrm{H_2O_2}) - [S^\circ(\mathrm{O_2}) + S^\circ(\mathrm{H_2})] \\ &= [1 \text{ mol } \mathrm{H_2O_2} \times 109.6 \text{ J}/(\text{mol} \cdot \text{K})] \\ &\quad - \{[1 \text{ mol } \mathrm{H_2} \times 130.7 \text{ J}/(\text{mol} \cdot \text{K})] + [1 \text{ mol } \mathrm{O_2} \times 205.2 \text{ J}/(\text{mol} \cdot \text{K})]\} \\ &= -226.3 \text{ J/K (per mole of } \mathrm{H_2O_2}) \end{aligned} \tag{8.6.27}$$

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 8.6.26,

$$\begin{aligned} \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ &= -187.78 \text{ kJ/mol} - (298.15 \text{ K})[-226.3 \text{ J}/(\text{mol} \cdot \text{K}) \times 1 \text{ kJ}/1000 \text{ J}] \\ &= -187.78 \text{ kJ/mol} + 67.47 \text{ kJ/mol} = -120.31 \text{ kJ/mol} \end{aligned} \tag{8.6.28}$$

The negative value of ΔG° indicates that the reaction is spontaneous as written. Because ΔS° and ΔH° for this reaction have the same sign, the sign of ΔG° 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 8.6.3

Calculate the standard free-energy change (ΔG°) at 25°C for the reaction

$$2H_2(g) + N_2(g) \rightleftharpoons N_2H_4(l)$$

. 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:

Video Solution

149.5 kJ/mol; no

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG° 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:

$$\Delta^o_f = \Delta H^o_f - T\Delta S^o_f \tag{8.6.29}$$

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:

$$\Delta G^o_{rxn} = \sum m\Delta G^o_f(products) - \sum n\Delta^o_f(reactants) \tag{8.6.30}$$

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG° 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.

✓ Example 8.6.4

Calculate ΔG° for the reaction of isooctane with oxygen gas to give carbon dioxide and water (described in Example 7). 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:

$$\mathrm{C_8H_{18}(l) + \frac{25}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)}$$

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,

$$\begin{aligned}
\Delta G^\circ &= [8\Delta G^\circ_{\mathrm{f}}(\mathrm{CO_2}) + 9\Delta G^\circ_{\mathrm{f}}(\mathrm{H_2O})] - \left[1\Delta G^\circ_{\mathrm{f}}(\mathrm{C_8H_{18}}) + \frac{25}{2}\Delta G^\circ_{\mathrm{f}}(\mathrm{O_2})\right] \\
&= [(8\text{ mol})(-394.4\text{ kJ/mol}) + (9\text{ mol})(-237.1\text{ kJ/mol})] \\
&\quad - \left[(1\text{ mol})(-353.2\text{ kJ/mol}) + \left(\frac{25}{2}\text{ mol}\right)(0\text{ kJ/mol})\right] \\
&= -4935.9\text{ kJ (per mol of }\mathrm{C_8H_{18}})
\end{aligned}$$

Because ΔG° 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° is largely determined by the ΔG°_f of the stable products: water and carbon dioxide.

Exercise 8.6.4

Calculate ΔG° 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

Video Solution

Calculated values of ΔG° 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° 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° at various temperatures, as long as no phase change occurs over the temperature range being considered.

Note

In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Example 8.6.5

Calculate (a) ΔG° 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
- $\Delta H^\circ_f (NH_3)$ = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, S° values, and ΔH°_f for NH_3

Asked for: ΔG° 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 8.6.26 to obtain ΔG° for the reaction.
C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation ??? to obtain ΔG for the reaction at 300°C.

Solution

A To calculate ΔG° for the reaction using Equation 8.6.26, 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:

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= 2S^\circ(\text{NH}_3) - [S^\circ(\text{N}_2) + 3S^\circ(\text{H}_2)] \\ &= [2\text{ mol NH}_3 \times 192.8\text{ J}/(\text{mol}\cdot\text{K})] \\ &\quad - \{[1\text{ mol N}_2 \times 191.6\text{ J}/(\text{mol}\cdot\text{K})] + [3\text{ mol H}_2 \times 130.7\text{ J}/(\text{mol}\cdot\text{K})]\} \\ &= -198.1\text{ J/K (per mole of N}_2)\end{aligned} \tag{8.6.31}$$

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 8.6.26

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ - T\Delta S^\circ = (-91.8\text{ kJ}) - (298\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) = -32.7\text{ kJ (per mole of N}_2)$$

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 ???:

$$\begin{aligned}\Delta G_{300^\circ\text{C}} &= \Delta H_{300^\circ\text{C}} - (573\text{ K})(\Delta S_{300^\circ\text{C}}) = \Delta H^\circ - (573\text{ K})\Delta S^\circ \\ &= (-91.8\text{ kJ}) - (573\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) = 21.7\text{ kJ (per mole of N}_2)\end{aligned}$$

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 8.6.5

Calculate

a. ΔG° and
b. $\Delta G_{750^\circ C}$

for the following reaction

$$2NO_{(g)} + O_{2\ (g)} \rightleftharpoons 2NO_{2\ (g)}$$

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°(O_2) = 205.2 J/(mol•K),
- S°(NO_2) = 240.1 J/(mol•K),
- ΔH°_f(NO_2) = 33.2 kJ/mol, and
- ΔH°_f (NO) = 91.3 kJ/mol.

Answer

a. −72.5 kJ/mol of O_2
b. 33.8 kJ/mol of O_2

Video Solution

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° = 0 in Equation 8.6.26, as illustrated in Example 8.6.4.

✓ Example 8.6.6

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 8.6.3 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° equal to zero in Equation 8.6.26 and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution

In Example 8.6.3, 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° = −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° equal to zero and rearranging Equation 8.6.26 to solve for T:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0 \tag{8.6.32}$$

$$\Delta H^\circ = T\Delta S^\circ \tag{8.6.33}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-91.8\text{ kJ})(1000\text{ J/kJ})}{-198.1\text{ J/K}} = 463\text{ K} \tag{8.6.34}$$

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 8.6.6

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.

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° for a reaction.

8.7: ΔG° and K as Functions of Temperature

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

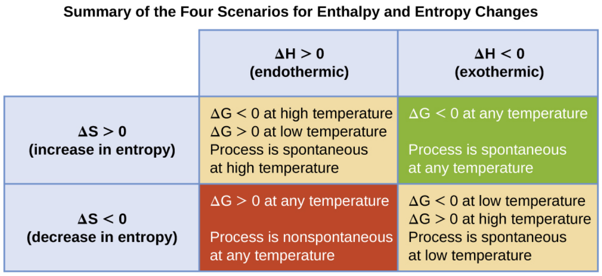
As was previously demonstrated, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. Likewise, some chemical reactions can also exhibit temperature dependent spontaneities. To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

$$\Delta G = \Delta H - T\Delta S \tag{8.7.1}$$

The spontaneity of a process, as reflected in the arithmetic sign of its free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both ΔH and ΔS are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, ΔG will be negative if the magnitude of the $T\Delta S$ term is greater than ΔH. If the $T\Delta S$ term is less than ΔH, the free energy change will be positive. Such a process is *spontaneous at high temperatures and nonspontaneous at low temperatures.*
2. **Both ΔH and ΔS are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, ΔG will be negative if the magnitude of the $T\Delta S$ term is less than ΔH. If the $T\Delta S$ term's magnitude is greater than ΔH, the free energy change will be positive. Such a process is *spontaneous at low temperatures and nonspontaneous at high temperatures.*
3. **ΔH is positive and ΔS is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, ΔG will be positive regardless of the temperature. Such a process is *nonspontaneous at all temperatures.*
4. **ΔH is negative and ΔS is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, ΔG will be negative regardless of the temperature. Such a process is *spontaneous at all temperatures.*

These four scenarios are summarized in Figure 8.7.1.



Summary of the Four Scenarios for Enthalpy and Entropy Changes

	ΔH > 0 (endothermic)	ΔH < 0 (exothermic)
ΔS > 0 (increase in entropy)	ΔG < 0 at high temperature ΔG > 0 at low temperature Process is spontaneous at high temperature	ΔG < 0 at any temperature Process is spontaneous at any temperature
ΔS < 0 (decrease in entropy)	ΔG > 0 at any temperature Process is nonspontaneous at any temperature	ΔG < 0 at low temperature ΔG > 0 at high temperature Process is spontaneous at low temperature

Figure 8.7.1: There are four possibilities regarding the signs of enthalpy and entropy changes.

Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2\,\mathrm{C}(s) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CO}(g)$$

How does the spontaneity of this process depend upon temperature?

Solution

Combustion processes are exothermic ($\Delta H < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S > 0$). The reaction is therefore spontaneous ($\Delta G < 0$) at all temperatures.

Exercise 8.7.3

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{Fe_2O_3}(s)$$

How does the spontaneity of this process depend upon temperature?

Answer

ΔH and ΔS are negative; the reaction is spontaneous at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of spontaneity, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is nonspontaneous at one temperature but spontaneous at another will necessarily undergo a change in “spontaneity” (as reflected by its ΔG) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which ΔG is plotted on the y axis versus T on the x axis:

$$\Delta G = \Delta H - T\Delta S \tag{8.7.2}$$

$$y = b + mx \tag{8.7.3}$$

Such a plot is shown in Figure 8.7.2. A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependent spontaneity as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the x-intercept of the line, that is, the value of T for which ΔG is zero:

$$\Delta G = 0 = \Delta H - T\Delta S \tag{8.7.4}$$

$$T = \frac{\Delta H}{\Delta S} \tag{8.7.5}$$

And so, saying a process is spontaneous at “high” or “low” temperatures means the temperature is above or below, respectively, that temperature at which ΔG for the process is zero. As noted earlier, this condition describes a system at equilibrium.

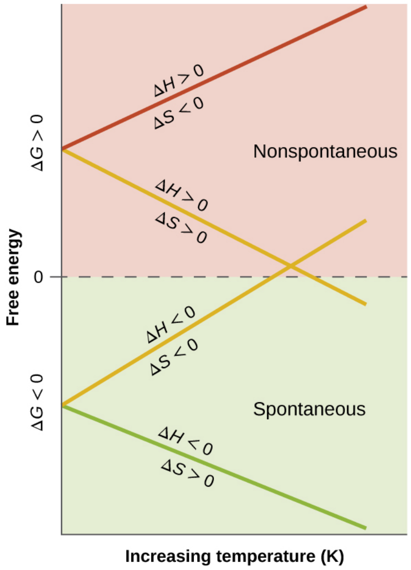


Figure 8.7.2: These plots show the variation in ΔG with temperature for the four possible combinations of arithmetic sign for ΔH and ΔS.

✓ Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its solid and liquid phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in Appendix G to estimate the boiling point of water.

Solution

The process of interest is the following phase change:

$$H_2O(l) \longrightarrow H_2O(g)$$

When this process is at equilibrium, $\Delta G = 0$, so the following is true:

$$0 = \Delta H^\circ - T\Delta S^\circ \qquad \text{or} \qquad T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Using the standard thermodynamic data from Appendix G,

$$\begin{aligned} \Delta H^\circ &= \Delta H_f^\circ(H_2O(g)) - \Delta H_f^\circ(H_2O(l)) \\ &= -241.82 \text{ kJ/mol} - (-285.83 \text{ kJ/mol}) = 44.01 \text{ kJ/mol} \end{aligned} \tag{8.7.6}$$

$$\begin{aligned} \Delta S^\circ &= \Delta S_{298}^\circ(H_2O(g)) - \Delta S_{298}^\circ(H_2O(l)) \\ &= 188.8 \text{ J/K}\cdot\text{mol} - 70.0 \text{ J/K}\cdot\text{mol} = 118.8 \text{ J/K}\cdot\text{mol} \end{aligned} \tag{8.7.7}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3 \text{ J/mol}}{118.8 \text{ J/K}\cdot\text{mol}} = 370.5 \text{ K} = 97.3 \ ^\circ\text{C}$$

The accepted value for water’s normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K (Appendix G). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

? Exercise 8.7.4

Use the information in Appendix G to estimate the boiling point of CS_2.

Answer

313 K (accepted value 319 K)

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 can be expressed as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{8.7.8}$$

Assuming ΔH° and ΔS° are **temperature independent,** for an exothermic reaction ($\Delta H^\circ < 0$), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction ($\Delta H^\circ > 0$), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 8.7.8 agrees 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 8.7.8 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 8.7.8 gives the following relationship at each temperature:

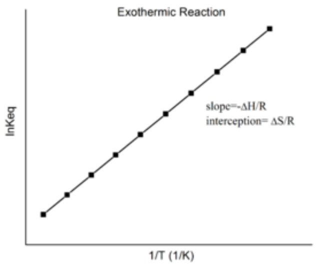
$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \tag{8.7.9}$$

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \tag{8.7.10}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{8.7.11}$$

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. The linear relation between $\ln K$ and the standard enthalpies and entropies in Equation 8.7.11 is known as the van't Hoff equation. It shows that a plot of $\ln K$ vs. $1/T$ should be a line with slope $-\Delta_r H^o/R$ and intercept $\Delta_r S^o/R$.



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Hence, these thermodynamic enthalpy and entropy changes for a reversible reaction can be determined from plotting $\ln K$ vs. $1/T$ data without the aid of calorimetry. Of course, the main assumption here is that $\Delta_r H^o$ and $\Delta_r S^o$ are only very weakly dependent on T, which is usually valid over a narrow temperature range.

Example 8.7.4

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C is $K_p = 5.4 \times 10^5$. What is K_p at 500°C? (Use the data from Example 10.)

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 kelvins. Then substitute appropriate values into Equation 8.7.11 to 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 8.7.11 we obtain the following:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{8.7.12}$$

$$= \frac{(-91.8 \text{ kJ})(1000 \text{ J/kJ})}{8.314 \text{ J/K}}\left(\frac{1}{298 \text{ K}} - \frac{1}{773 \text{ K}}\right) = -22.8 \tag{8.7.13}$$

$$\frac{K_2}{K_1} = 1.3 \times 10^{-10} \tag{8.7.14}$$

$$K_2 = (5.4 \times 10^5)(1.3 \times 10^{-10}) = 7.0 \times 10^{-5} \tag{8.7.15}$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

Exercise 8.7.4

In the exercise in Example 8.7.3, you calculated $K_p = 2.2 \times 10^{12}$ for the reaction of NO with O_2 to give NO_2 at 25°C. Use the ΔH°_f values in the exercise in Example 10 to calculate K_p for this reaction at 1000°C.

Answer: 5.6×10^{-4}

The Van't Hoff Equation: https://youtu.be/4vk6idAXp_A

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 $\Delta G^\circ < 0$, then K or $K_p > 1$, and products are favored over reactants. If $\Delta G^\circ > 0$, then K or $K_p < 1$, and reactants are favored over products. If $\Delta G^\circ = 0$, 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

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8.8: Coupled Reactions

Learning Objectives

Endergonic reactions can also be pushed by coupling them to another reaction, which is strongly exergonic, often through shared intermediates.

Many chemicals' reactions are *endergonic* (i.e., not spontaneous ($\Delta G > 0$)) and require energy to be externally applied to occur. However, these reaction can be *coupled* to a separate, *exergonic* (thermodynamically favorable $\Delta G < 0$) reactions that 'drive' the thermodynamically unfavorable one by coupling or 'mechanistically joining' the two reactions often via a share intermediate. Since Gibbs Energy is a state function, the ΔG values for each half-reaction may be summed, to yield the combined ΔG of the coupled reaction.

One simple example of the coupling of reaction is the decomposition of calcium carbonate:

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)} \qquad \Delta G^o = 130.40\ kJ/mol \tag{8.8.1}$$

The strongly positive ΔG for this reaction is reactant-favored. If the temperature is raised above 837 ºC, this reaction becomes spontaneous and favors the products. Now, let's consider a second and completely different reaction that can be coupled ot this reaction. The combustion of coal released by burning the coal $\Delta G^o = -394.36\ kJ/mol$ is greater than the energy required to decompose calcium carbonate ($\Delta G^o = 130.40\ kJ/mo$).

$$C_{(s)} + O_2 \rightleftharpoons CO_{2(g)} \qquad \Delta G^o = -394.36\ kJ/mol \tag{8.8.2}$$

If reactions 8.8.1 and 8.8.2 were added

$$CaCO_{3(s)} + C_{(s)} + O_2 \rightleftharpoons CaO_{(s)} + 2CO_{[}2(g) \quad \Delta G^o = -263.96\ kJ/mol \tag{8.8.3}$$

and then Hess's Law were applied, the combined reaction (Equation 8.8.3) is product-favored with $\Delta G^o = -263.96\ kJ/mol$. This is because the reactant-favored reaction (Equation 8.8.2) is linked to a strong spontaneous reaction so that both reactions yield products. Notice that the ΔG for the coupled reaction is the sum of the constituent reactions; this is a consequence of Gibbs energy being a state function:

$$\Delta G^o = 130.40\ kJ/mol + -394.36\ kJ/mol = -263.96\ kJ/mol \tag{8.8.4}$$

Coupled Reactions in Biology

This is a common feature in biological systems where some enzyme-catalyzed reactions are interpretable as two coupled half-reactions, one spontaneous and the other non-spontaneous. Organisms often the hydrolysis of **ATP** (adenosine triphosphate) to generate **ADP** (adenosine diphosphate) as the spontaneous coupling reaction (Figure 8.8.1).

$$ATP + H_2O \rightleftharpoons ADP + P_i \tag{8.8.5}$$

- P_i is inorganic phosphate ion

The phosphoanhydride bonds formed by ejecting water between two phosphate group of ATP exhibit a large negative $-\Delta G$ of hydrolysis and are thus often termed "high energy" bonds. However, as with all bonds, energy is requires to break these bonds, but the thermodynamic Gibbs energy difference is strongly "energy releasing" when including the solvation thermodynamics of the phosphate ions; ΔG for this reaction is - 31 kJ/mol.

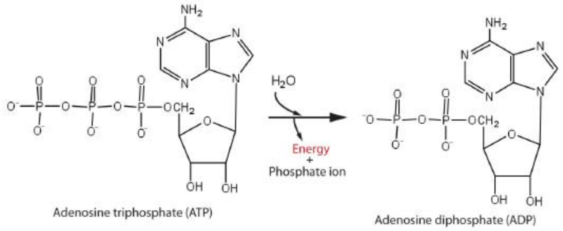

Figure 8.8.1*: Hydrolysis of ATP to Form ADP*

ATP is the major 'energy' molecule produced by metabolism, and it serves as a sort of 'energy source' in cell: ATP is dispatched to wherever a non-spontaneous reaction needs to occurs so that the two reactions are coupled so that the overall reaction is thermodynamically favored.

✓ Example 8.8.1: Phosphorylating Carboxylic Acids

Aldehydes $RCHO$ are organic compounds that can be oxidized to generate carboxylic acids and nicotinamide adenine dinucleotide (NAD) is a coenzyme found in all living cells and in the reduced form, NAD^+, it acts as an oxidizing agent that can accept electrons from other molecules.

The NAD$^+$-linked oxidation of an aldehyde is practically irreversible with an equilibrium that strongly favors the products ($\Delta G >> 0$:

$$RCHO + NAD^+ + H_2O \rightleftharpoons RCOOH + NADH + H^+ \tag{8.8.6}$$

The position of equilibrium for phosphorylating carboxylic acids lies very much to the left:

$$RCOOH + P_i \rightleftharpoons RC(=O)(O - P_i) + H_2O \tag{8.8.7}$$

- (P_i\) is inorganic phosphate ion.

The non-spontaneous formation of a phosphorylated carboxylic acid can be driven by coupling it to the (spontaneous) NAD$^+$-linked oxidation of an aldehyde?

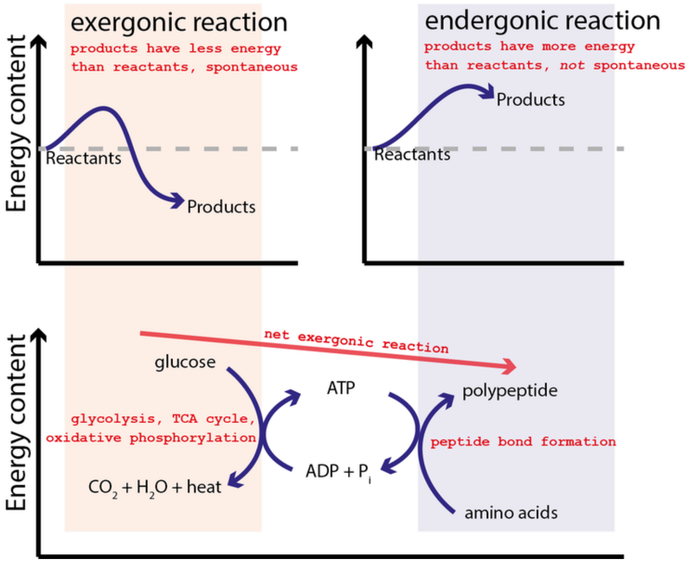

Figure 8.8.2: A reaction will not proceed spontaneously unless the products of the reaction have lower energy than the reactants. This is called an exergonic reactions. A reaction where the products have higher energy than the reactions (energonic reaction) can only proceed when there is an input of energy. Exergonic reactions like burning of glucose drives ATP synthesis. The ATP molecules are used to power other endergonic reactions like protein synthesis. from Wikipedia (Muessig).

Similarly, ATP hydrolysis can be used to combine amino acids together to generate polypeptides (and proteins) as graphically illustrated by Figure 8.8.2. In this case, the reverse of Equation 8.8.5 is initially coupled to the oxidizing glucose by oxygen

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \tag{8.8.8}$$

Reaction 8.8.8 is strongly spontaneous with $\Delta G = -2880\ kJ/mol$ or close to 100x greater energy capability than the hydrolysis of ATP in Equation 8.8.5. Hence, the equilibrium for this reaction so strongly favors the products that a single arrow is typically used in the chemical equation as it is essential irreversible. It may not be surpising that glucose and all sugars are very energetic moleculess since they are the primary energy source for life.

References

1. Damitio , J., Smith , G., Meany , J. E., Pocker, Y. (1992). A comparative study of the enolization of pyruvate and the reversible dehydration of pyruvate hydrate *J. Am. Chem. Soc.*, **114**, 3081–3087

2. Pocker, Y., Meany, J. E., Nist, B. J., & Zadorojny, C. (1969) The Reversible Hydration of Pyruvic Acid. I. Equilibrium Studies. *J. Phys. Chem.* **76**, 2879 – 2882.
3. Waslh, C. (1979) *Enzymatic Reaction Mechanisms*. W.H. Freeman & Co.

Summary

Two (or more) reactions may be combined such that a spontaneous reaction may be made 'drive' an nonspontaneous one. Such reactions may be considered *coupled*. Changes in Gibbs energy of the coupled reactions are additive.

Contributors and Attributions

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8.E: Chemical Thermodynamics (Exercises)

Spontaneity Exercises

1. What is a spontaneous reaction?

Answer

A reaction has a natural tendency to occur and takes place without the continual input of energy from an external source.

2. What is a nonspontaneous reaction?

3. Indicate whether the following processes are spontaneous or nonspontaneous.

- Liquid water freezing at a temperature below its freezing point
- Liquid water freezing at a temperature above its freezing point
- The combustion of gasoline
- A ball thrown into the air
- A raindrop falling to the ground
- Iron rusting in a moist atmosphere

Answer

spontaneous; nonspontaneous; spontaneous; nonspontaneous; spontaneous; spontaneous

4. A helium-filled balloon spontaneously deflates overnight as He atoms diffuse through the wall of the balloon. Describe the redistribution of matter and/or energy that accompanies this process.

5. Many plastic materials are organic polymers that contain carbon and hydrogen. The oxidation of these plastics in air to form carbon dioxide and water is a spontaneous process; however, plastic materials tend to persist in the environment. Explain.

Answer

Although the oxidation of plastics is spontaneous, the rate of oxidation is very slow. Plastics are therefore kinetically stable and do not decompose appreciably even over relatively long periods of time

Entropy Exercises

6. In the below Figure all possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, Δ*S*, if the particles are initially evenly distributed between the two boxes, but upon redistribution all end up in Box (b).

CNX_Chem_16_02_Microstates.jpg

7. In Figure all of the possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, Δ*S*, for the system when it is converted from distribution to distribution (d).

CNX_Chem_16_02_Microstates.jpg

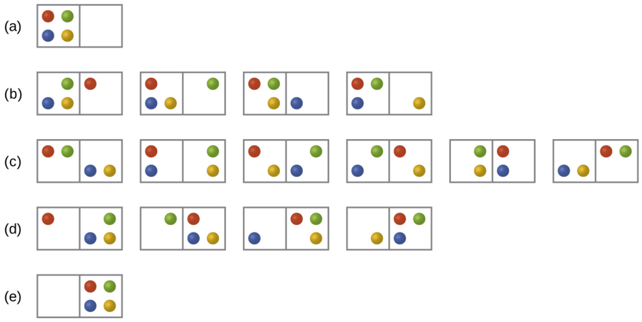
Answer

There are four initial microstates and four final microstates.

ΔS=klnWfWi=1.38×10−23J/K×ln44=0(16.E.1)(16.E.1)ΔS=klnWfWi=1.38×10−23J/K×ln44=0

8. How does the process described in the previous item relate to the system shown in [link]?

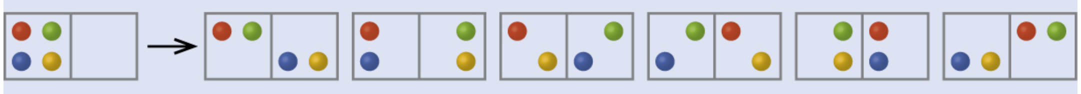
9. Consider a system similar to the one below, except that it contains six particles instead of four. What is the probability of having all the particles in only one of the two boxes in the case? Compare this with the similar probability for the system of four particles that we have derived to be equal to 1818. What does this comparison tell us about even larger systems?



Answer

The probability for all the particles to be on one side is 132132. This probability is noticeably lower than the 1818 result for the four-particle system. The conclusion we can make is that the probability for all the particles to stay in only one part of the system will decrease rapidly as the number of particles increases, and, for instance, the probability for all molecules of gas to gather in only one side of a room at room temperature and pressure is negligible since the number of gas molecules in the room is very large.

10. Consider the system shown in Figure. What is the change in entropy for the process where the energy is initially associated only with particle A, but in the final state the energy is distributed between two different particles?



11. Consider the system shown in Figure. What is the change in entropy for the process where the energy is initially associated with particles A and B, and the energy is distributed between two particles in different boxes (one in A-B, the other in C-D)?

Answer

There is only one initial state. For the final state, the energy can be contained in pairs A-C, A-D, B-C, or B-D. Thus, there are four final possible states.

$$\Delta S = k\ln\left(\frac{W_f}{W_i}\right) = 1.38\times10^{-23} J/K \times \ln\left(\frac{4}{1}\right) = 1.91\times10^{-23} J/K \tag{16.E.2}$$

(16.E.2)$\Delta S = k\ln\left(\frac{W_f}{W_i}\right) = 1.38\times10^{-23} J/K \times \ln\left(\frac{4}{1}\right) = 1.91\times10^{-23} J/K$

12. Arrange the following sets of systems in order of increasing entropy. Assume one mole of each substance and the same temperature for each member of a set.

1. $H_2(g)$, $HBrO_4(g)$, $HBr(g)$
2. $H_2O(l)$, $H_2O(g)$, $H_2O(s)$
3. $He(g)$, $Cl_2(g)$, $P_4(g)$

13. At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2. Explain.

Answer

The masses of these molecules would suggest the opposite trend in their entropies. The observed trend is a result of the more significant variation of entropy with a physical state. At room temperature, I_2 is a solid, Br_2 is a liquid, and Cl_2 is a gas.

14. Consider two processes: sublimation of $I_2(s)$ and melting of $I_2(s)$ (Note: the latter process can occur at the same temperature but somewhat higher pressure).

$$I_2(s) \longrightarrow I_2(g)$$

$$I_2(s) \longrightarrow I_2(l)$$

Is ΔS positive or negative in these processes? In which of the processes will the magnitude of the entropy change be greater?

15. Indicate which substance in the given pairs has the higher entropy value. Explain your choices.

1. $C_2H_5OH(l)$ or $C_3H_7OH(l)$

2. $C_2H_5OH(l)$ or $C_2H_5OH(g)$
3. 2H or $H(g)$

Answer

$C_3H_7OH(l)$ as it is a larger molecule (more complex and more massive), and so more microstates describing its motions are available at any given temperature.

$C_2H_5OH(g)$ as it is in the gaseous state.

$2H(g)$, since entropy is an extensive property, and so two H atoms (or two moles of H atoms) possess twice as much entropy as one atom (or one mole of atoms).

16. Predict the sign of the entropy change for the following processes:

1. An ice cube is warmed to near its melting point.
2. Exhaled breath forms fog on a cold morning.
3. Snow melts.

17. Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

1. $Pb2+(aq)+S2-(aq)\longrightarrow PbS(s)$
2. $2Fe(s)+3O2(g)\longrightarrow Fe2O3(s)$
3. $2C6H14(l)+19O2(g)\longrightarrow 14H2O(g)+12CO2(g)$

Answer

1. Negative. The relatively ordered solid precipitating decreases the number of mobile ions in solution.
2. Negative. There is a net loss of three moles of gas from reactants to products.
3. Positive. There is a net increase of seven moles of gas from reactants to products.

18. Write the balanced chemical equation for the combustion of methane, $CH_4(g)$, to give carbon dioxide and water vapor. Explain why it is difficult to predict whether ΔS is positive or negative for this chemical reaction.

19. Write the balanced chemical equation for the combustion of benzene, $C_6H_6(l)$, to give carbon dioxide and water vapor. Would you expect ΔS to be positive or negative in this process?

Answer

$C6H6(l)+7.5O2(g)\longrightarrow 3H2O(g)+6CO2(g)$

There are 7.5 moles of gas initially, and 3 + 6 = 9 moles of gas in the end. Therefore, it is likely that the entropy increases as a result of this reaction, and ΔS is positive.

The Second and Third law

20. What is the difference between ΔS, $\Delta S°$, and $\Delta S∘298\Delta S298∘$ for a chemical change?

21. Calculate $\Delta S∘298\Delta S298∘$ for the following changes.

a. $SnCl4(l)\longrightarrow SnCl4(g)$

b. $CS2(g)\longrightarrow CS2(l)$

c. $Cu(s)\longrightarrow Cu(g)$

d. $H2O(l)\longrightarrow H2O(g)$

e. $2H2(g)+O2(g)\longrightarrow 2H2O(l)$

f. $2HCl(g)+Pb(s)\longrightarrow PbCl2(s)+H2(g)$

g. $Zn(s)+CuSO4(s)\longrightarrow Cu(s)+ZnSO4(s)$

Answer

a. 107 J/K; b. −86.4 J/K; c. 133.2 J/K; d. 118.8 J/K; e. −326.6 J/K; f. −171.9 J/K; g. −7.2 J/K

22. Determine the entropy change for the combustion of liquid ethanol, C_2H_5OH, under standard state conditions to give gaseous carbon dioxide and liquid water.

23. Determine the entropy change for the combustion of gaseous propane, C_3H_8, under standard state conditions to give gaseous carbon dioxide and water.

Answer

100.6 J/K

24. “Thermite” reactions have been used for welding metal parts such as railway rails and in metal refining. One such thermite reaction is:

$Fe2O3(s)+2Al(s)\longrightarrow Al2O3(s)+2Fe(s)$

Is the reaction spontaneous at room temperature under standard conditions? During the reaction, the surroundings absorb 851.8 kJ/mol of heat.

25. Using the relevant $S298\circ$ values listed in Appendix G, calculate $S298\circ$ for the following changes:

1. $N2(g)+3H2(g)\longrightarrow 2NH3(g)$
2. $N2(g)+52O2(g)\longrightarrow N2O5(g)$

Answer

−198.1 J/K; −348.9 J/K

26. From the following information, determine $\Delta S298\circ$ for the following:

- $N(g)+O(g)\longrightarrow NO(g)\Delta S298\circ=?$
- $N2(g)+O2(g)\longrightarrow 2NO(g)\Delta S298\circ=24.8J/K$
- $N2(g)\longrightarrow 2N(g)\Delta S298\circ=115.0J/K$
- $O2(g)\longrightarrow 2O(g)\Delta S298\circ=117.0J/K$

27. Use the standard entropy data in Appendix G to determine the change in entropy for each of the reactions listed in [link]. All are run under standard state conditions and 25 °C.

Answer

2.86 J/K; 24.8 J/K; −113.2 J/K; −24.7 J/K; 15.5 J/K; 290.0 J/K

Free Energy

28. What is the difference between ΔG, $\Delta G°$, and $\Delta G\circ 298\Delta G298\circ$ for a chemical change?

29. A reactions has $\Delta H\circ 298\Delta H298\circ$ = 100 kJ/mol and $\Delta S\circ 298=250$ J/mol·K$\Delta S298\circ=250$ J/mol·K. Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

Answer

The reaction is nonspontaneous at room temperature. Above 400 K, ΔG will become negative, and the reaction will become spontaneous.

30. Explain what happens as a reaction starts with $\Delta G < 0$ (negative) and reaches the point where $\Delta G = 0$.

31. Use the standard free energy of formation data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

- $MnO2(s)\longrightarrow Mn(s)+O2(g)$
- $H2(g)+Br2(l)\longrightarrow 2HBr(g)$
- $Cu(s)+S(g)\longrightarrow CuS(s)$
- $2LiOH(s)+CO2(g)\longrightarrow Li2CO3(s)+H2O(g)$
- $CH4(g)+O2(g)\longrightarrow C(s,graphite)+2H2O(g)$
- $CS2(g)+3Cl2(g)\longrightarrow CCl4(g)+S2Cl2(g)$

Answer

465.1 kJ nonspontaneous; −106.86 kJ spontaneous; −53.6 kJ spontaneous; −83.4 kJ spontaneous; −406.7 kJ spontaneous; −30.0 kJ spontaneous

32. Use the standard free energy data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

- $C(s,graphite)+O2(g)\longrightarrow CO2(g)$
- $O2(g)+N2(g)\longrightarrow 2NO(g)$
- $2Cu(s)+S(g)\longrightarrow Cu2S(s)$
- $CaO(s)+H2O(l)\longrightarrow Ca(OH)2(s)$
- $Fe2O3(s)+3CO(g)\longrightarrow 2Fe(s)+3CO2(g)$
- $CaSO4\cdot 2H2O(s)\longrightarrow CaSO4(s)+2H2O(g)$

33. Determine the standard free energy of formation, $\Delta Gf\circ$, for phosphoric acid. How does your calculated result compare to the value in Appendix G? Explain.

Answer

−1124.3 kJ/mol for the standard free energy change. The calculation agrees with the value in Appendix G because free energy is a state function (just like the enthalpy and entropy), so its change depends only on the initial and final states, not the path between them.

34. Is the formation of ozone ($O_3(g)$) from oxygen ($O_2(g)$) spontaneous at room temperature under standard state conditions?

35. Consider the decomposition of red mercury(II) oxide under standard state conditions.

$2HgO(s,red)\longrightarrow 2Hg(l)+O2(g)(16.E.10)(16.E.10)2HgO(s,red)\longrightarrow 2Hg(l)+O2(g)$

Is the decomposition spontaneous under standard state conditions? Above what temperature does the reaction become spontaneous?

Answer

The reaction is nonspontaneous; Above 566 °C the process is spontaneous.

36. Among other things, an ideal fuel for the control thrusters of a space vehicle should decompose in a spontaneous exothermic reaction when exposed to the appropriate catalyst. Evaluate the following substances under standard state conditions as suitable candidates for fuels.

1. Ammonia: $2NH3(g)\longrightarrow N2(g)+3H2(g)$
2. Diborane: $B2H6(g)\longrightarrow 2B(g)+3H2(g)$
3. Hydrazine: $N2H4(g)\longrightarrow N2(g)+2H2(g)$
4. Hydrogen peroxide: $H2O2(l)\longrightarrow H2O(g)+12O2(g)$

37. Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

1. $N2(g)+O2(g)\longrightarrow 2NO(g) T=2000°C\ Kp=4.1\times 10−4$
2. $H2(g)+I2(g)\longrightarrow 2HI(g) T=400°C\ Kp=50.0$
3. $CO2(g)+H2(g)\longrightarrow CO(g)+H2O(g)\ T=980°C\ Kp=1.67$
4. $CaCO3(s)\longrightarrow CaO(s)+CO2(g)\ T=900°C\ Kp=1.04$
5. $HF(aq)+H2O(l)\longrightarrow H3O+(aq)+F−(aq)\ T=25°C\ Kp=7.2\times 10−4$
6. $AgBr(s)\longrightarrow Ag+(aq)+Br−(aq)\ T=25°C\ Kp=3.3\times 10−13$

Answer

1.5×10^2 kJ; −21.9 kJ; −5.34 kJ; −0.383 kJ; 18 kJ; 71 kJ

38. Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

1. $Cl2(g)+Br2(g)\longrightarrow 2BrCl(g)\ T=25°C\ Kp=4.7\times 10−2$
2. $2SO2(g)+O2(g)\rightleftharpoons 2SO3(g)\ T=500°C\ Kp=48.2$

3. $H_2O(l) \rightleftharpoons H_2O(g)$ T=60°C $K_p=0.196 atm$
4. $CoO(s)+CO(g) \rightleftharpoons Co(s)+CO_2(g)$ T=550°C $K_p=4.90 \times 102$
5. $CH_3NH_2(aq)+H_2O(l) \longrightarrow CH_3NH_3^+(aq)+OH^-(aq)$ T=25°C $K_p=4.4 \times 10-4$
6. $PbI_2(s) \longrightarrow Pb^{2+}(aq)+2I^-(aq)$ T=25°C $K_p=8.7 \times 10-9$

39. Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of Δ*G*° given.

- $O_2(g)+2F_2(g) \longrightarrow 2OF_2(g) \Delta G° = -9.2 kJ$
- $I_2(s)+Br_2(l) \longrightarrow 2IBr(g) \Delta G° = 7.3 kJ$
- $2LiOH(s)+CO_2(g) \longrightarrow Li_2CO_3(s)+H_2O(g) \Delta G° = -79 kJ$
- $N_2O_3(g) \longrightarrow NO(g)+NO_2(g) \Delta G° = -1.6 kJ$
- $SnCl_4(l) \longrightarrow SnCl_4(l) \Delta G° = 8.0 kJ$

Answer

K = 41; K = 0.053; $K = 6.9 \times 10^{13}$; K = 1.9; K = 0.04

40. Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of Δ*G*° given.

- $I_2(s)+Cl_2(g) \longrightarrow 2ICl(g) \Delta G° = -10.88 kJ$
- $H_2(g)+I_2(s) \longrightarrow 2HI(g) \Delta G° = 3.4 kJ$
- $CS_2(g)+3Cl_2(g) \longrightarrow CCl_4(g)+S_2Cl_2(g) \Delta G° = -39 kJ$
- $2SO_2(g)+O_2(g) \longrightarrow 2SO_3(g) \Delta G° = -141.82 kJ$
- $CS_2(g) \longrightarrow CS_2(l) \Delta G° = -1.88 kJ$

41. Calculate the equilibrium constant at the temperature given.

- $O_2(g)+2F_2(g) \longrightarrow 2F_2O(g)$ (T=100°C)
- $I_2(s)+Br_2(l) \longrightarrow 2IBr(g)$ (T=0.0°C)
- $2LiOH(s)+CO_2(g) \longrightarrow Li_2CO_3(s)+H_2O(g)$ (T=575°C)
- $N_2O_3(g) \longrightarrow NO(g)+NO_2(g)$ (T=−10.0°C)
- $SnCl_4(l) \longrightarrow SnCl_4(g)$ (T=200°C)

Answer

In each of the following, the value of Δ*G* is not given at the temperature of the reaction. Therefore, we must calculate Δ*G*° from the values Δ*H*° and Δ*S*° and then calculate Δ*G* from the relation $\Delta G° = \Delta H° - T\Delta S°$.

K = 1.29; $K = 2.51 \times 10^{-3}$; $K = 4.83 \times 10^{3}$; K = 0.219; K = 16.1

42. Calculate the equilibrium constant at the temperature given.

- $I_2(s)+Cl_2(g) \longrightarrow 2ICl(g)$ (T=100°C)
- $H_2(g)+I_2(s) \longrightarrow 2HI(g)$ (T=0.0°C)
- $CS_2(g)+3Cl_2(g) \longrightarrow CCl_4(g)+S_2Cl_2(g)$ (T=125°C)
- $2SO_2(g)+O_2(g) \longrightarrow 2SO_3(g)$ (T=675°C)
- $CS_2(g) \longrightarrow CS_2(l)$ (T=90°C)

43. Consider the following reaction at 298 K:

$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad K_P=0.142$

What is the standard free energy change at this temperature? Describe what happens to the initial system, where the reactants and products are in standard states, as it approaches equilibrium.

Answer

The standard free energy change is $\Delta G{\circ}298=-RTlnK=4.84 kJ/mol \Delta G298{\circ}=-RTlnK=4.84 kJ/mol$. When reactants and products are in their standard states (1 bar or 1 atm), Q = 1. As the reaction proceeds toward equilibrium, the reaction shifts left (the amount of products drops while the amount of reactants increases): Q < 1, and $\Delta G298$ becomes less positive as it approaches zero. At equilibrium, $Q = K$, and ΔG = 0.

44. Determine the normal boiling point (in kelvin) of dichloroethane, CH_2Cl_2. Find the actual boiling point using the Internet or some other source, and calculate the percent error in the temperature. Explain the differences, if any, between the two values.

45. Under what conditions is $N2O3(g)\longrightarrow NO(g)+NO2(g)$ spontaneous?

Answer

The reaction will be spontaneous at temperatures greater than 287 K.

46. At room temperature, the equilibrium constant (K_w) for the self-ionization of water is 1.00×10^{-14}. Using this information, calculate the standard free energy change for the aqueous reaction of hydrogen ion with hydroxide ion to produce water. (Hint: The reaction is the reverse of the self-ionization reaction.)

47. Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction $2H2S(g)+SO2(g)\rightleftharpoons 38S8(s,rhombic)+2H2O(l)$. What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

Answer

$K = 5.35 \times 10^{15}$

The process is exothermic.

48. Consider the decomposition of $CaCO_3(s)$ into $CaO(s)$ and $CO_2(g)$. What is the equilibrium partial pressure of CO_2 at room temperature?

49. In the laboratory, hydrogen chloride ($HCl(g)$) and ammonia ($NH_3(g)$) often escape from bottles of their solutions and react to form the ammonium chloride ($NH_4Cl(s)$), the white glaze often seen on glassware. Assuming that the number of moles of each gas that escapes into the room is the same, what is the maximum partial pressure of HCl and NH_3 in the laboratory at room temperature? (Hint: The partial pressures will be equal and are at their maximum value when at equilibrium.)

Answer

1.0×10^{-8} atm. This is the maximum pressure of the gases under the stated conditions.

50. Benzene can be prepared from acetylene. $3C2H2(g)\rightleftharpoons C6H6(g)$. Determine the equilibrium constant at 25 °C and at 850 °C. Is the reaction spontaneous at either of these temperatures? Why is all acetylene not found as benzene?

51. Carbon dioxide decomposes into CO and O_2 at elevated temperatures. What is the equilibrium partial pressure of oxygen in a sample at 1000 °C for which the initial pressure of CO_2 was 1.15 atm?

Answer

$x=1.29\times10-5\ atm=PO2$

52. Carbon tetrachloride, an important industrial solvent, is prepared by the chlorination of methane at 850 K.

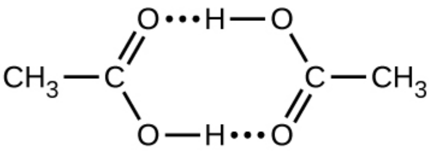
$CH4(g)+4Cl2(g)\longrightarrow CCl4(g)+4HCl(g)$

What is the equilibrium constant for the reaction at 850 K? Would the reaction vessel need to be heated or cooled to keep the temperature of the reaction constant?

53. Acetic acid, CH_3CO_2H, can form a dimer, $(CH_3CO_2H)_2$, in the gas phase.

$2CH3CO2H(g)\longrightarrow (CH3CO2H)2(g)$

The dimer is held together by two hydrogen bonds with a total strength of 66.5 kJ per mole of dimer.



At 25 °C, the equilibrium constant for the dimerization is 1.3×10^3 (pressure in atm). What is $\Delta S°$ for the reaction?

Answer

−0.16 kJ

54. Nitric acid, HNO_3, can be prepared by the following sequence of reactions:

4NH3(g)+5O2(g)⟶4NO(g)+6H2O(g)

2NO(g)+O2(g)⟶2NO2(g)

3NO2(g)+H2O(l)⟶2HNO3(l)+NO(g)

How much heat is evolved when 1 mol of $NH_3(g)$ is converted to $HNO_3(l)$? Assume standard states at 25 °C.

55. Determine ΔG for the following reactions.

(a) Antimony pentachloride decomposes at 448 °C. The reaction is:

SbCl5(g)⟶SbCl3(g)+Cl2(g)

An equilibrium mixture in a 5.00 L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2.

(b) Chlorine molecules dissociate according to this reaction:

Cl2(g)⟶2Cl(g)

1.00% of Cl_2 molecules dissociate at 975 K and a pressure of 1.00 atm.

Answer

(a) −22.1 kJ; (b)61.6 kJ/mol

56. Given that the ΔG∘fΔGf∘ for $Pb^{2+}(aq)$ and $Cl^{-}(aq)$ is −24.3 kJ/mole and −131.2 kJ/mole respectively, determine the solubility product, K_{sp}, for $PbCl_2(s)$.

57. Determine the standard free energy change, ΔGf∘, for the formation of $S^{2-}(aq)$ given that the ΔGf∘ for $Ag^{+}(aq)$ and $Ag_2S(s)$ are 77.1 k/mole and −39.5 kJ/mole respectively, and the solubility product for $Ag_2S(s)$ is 8×10^{-51}.

Answer

90 kJ/mol

58. Determine the standard enthalpy change, entropy change, and free energy change for the conversion of diamond to graphite. Discuss the spontaneity of the conversion with respect to the enthalpy and entropy changes. Explain why diamond spontaneously changing into graphite is not observed.

59. The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.

H2O(l)⇌H2O(g)ΔG298∘=8.58kJ

a. Is the evaporation of water under standard thermodynamic conditions spontaneous?

b. Determine the equilibrium constant, K_P, for this physical process.

c. By calculating ΔG, determine if the evaporation of water at 298 K is spontaneous when the partial pressure of water, PH2OPH2O, is 0.011 atm.

d. If the evaporation of water were always nonspontaneous at room temperature, wet laundry would never dry when placed outside. In order for laundry to dry, what must be the value of PH2O in the air?

Answer

a. Under standard thermodynamic conditions, the evaporation is nonspontaneous; b. K_p = 0.031; c. The evaporation of water is spontaneous; PH2O must always be less than K_p or less than 0.031 atm. d. 0.031 atm represents air saturated with water vapor at 25 °C, or 100% humidity.

60. In glycolysis, the reaction of glucose (Glu) to form glucose-6-phosphate (G6P) requires ATP to be present as described by the following equation:

Glu+ATP⟶G6P+ADPΔG298∘=−17kJ

In this process, ATP becomes ADP summarized by the following equation:

$ATP\longrightarrow ADP\Delta G298\circ=-30kJ$

Determine the standard free energy change for the following reaction, and explain why ATP is necessary to drive this process:

$Glu\longrightarrow G6P\Delta G298\circ=?$

61. One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):

$G6P\rightleftharpoons F6P\Delta G298\circ=1.7kJ$

a. Is the reaction spontaneous or nonspontaneous under standard thermodynamic conditions?

b. Standard thermodynamic conditions imply the concentrations of G6P and F6P to be 1 *M*, however, in a typical cell, they are not even close to these values. Calculate Δ*G* when the concentrations of G6P and F6P are 120 μ*M* and 28 μ*M* respectively, and discuss the spontaneity of the forward reaction under these conditions. Assume the temperature is 37 °C.

Answer

a. Nonspontaneous as $\Delta G298\circ>0$;

b. $\Delta G298\circ=-RTlnK$, $\Delta G=1.7\times103+(8.314\times335\times ln28128)=-2.5kJ$. The forward reaction to produce F6P is spontaneous under these conditions.

62. Without doing a numerical calculation, determine which of the following will reduce the free energy change for the reaction, that is, make it less positive or more negative, when the temperature is increased. Explain.

a. $N2(g)+3H2(g)\longrightarrow 2NH3(g)$

b. $HCl(g)+NH3(g)\longrightarrow NH4Cl(s)$

c. $(NH4)2Cr2O7(s)\longrightarrow Cr2O3(s)+4H2O(g)+N2(g)$

d. $2Fe(s)+3O2(g)\longrightarrow Fe2O3(s)$

When ammonium chloride is added to water and stirred, it dissolves spontaneously and the resulting solution feels cold. Without doing any calculations, deduce the signs of Δ*G*, Δ*H*, and Δ*S* for this process, and justify your choices.

Answer

Δ*G* is negative as the process is spontaneous. Δ*H* is positive as with the solution becoming cold, the dissolving must be endothermic. Δ*S* must be positive as this drives the process, and it is expected for the dissolution of any soluble ionic compound.

63. An important source of copper is from the copper ore, chalcocite, a form of copper(I) sulfide. When heated, the Cu_2S decomposes to form copper and sulfur described by the following equation:

$Cu2S(s)\longrightarrow Cu(s)+S(s)$

a. Determine $\Delta G\circ298\Delta G298\circ$ for the decomposition of $Cu_2S(s)$.

b. The reaction of sulfur with oxygen yields sulfur dioxide as the only product. Write an equation that describes this reaction, and determine $\Delta G\circ298\Delta G298\circ$ for the process.

c. The production of copper from chalcocite is performed by roasting the Cu_2S in air to produce the Cu. By combining the equations from Parts (a) and (b), write the equation that describes the roasting of the chalcocite, and explain why coupling these reactions together makes for a more efficient process for the production of the copper.

64. What happens to $\Delta G\circ298\Delta G298\circ$ (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

a. $S(s)+O2(g)\longrightarrow SO2(g)$

b. $2SO2(g)+O2(g)\longrightarrow SO3(g)$

c. $HgO(s)\longrightarrow Hg(l)+O2(g)$

Answer

a. Increasing P_{O2} will shift the equilibrium toward the products, which increases the value of *K*. ΔG°_{298} therefore becomes more negative.

b. Increasing P_{O2} will shift the equilibrium toward the products, which increases the value of *K*. ΔG°_{298} therefore becomes more negative.

c. Increasing P_{O2} will shift the equilibrium the reactants, which decreases the value of *K*. ΔG°_{298} therefore becomes more positive.

CHAPTER OVERVIEW

9: Electrochemistry

Electrochemistry deals with chemical reactions that produce electricity and the changes associated with the passage of electrical current through matter. The reactions involve electron transfer, and so they are oxidation-reduction (or redox) reactions. Many metals may be purified or electroplated using electrochemical methods. Devices such as automobiles, smartphones, electronic tablets, watches, pacemakers, and many others use batteries for power. Batteries use chemical reactions that produce electricity spontaneously and that can be converted into useful work. All electrochemical systems involve the transfer of electrons in a reacting system. In many systems, the reactions occur in a region known as the cell, where the transfer of electrons occurs at electrodes.

Contributors and Attributions

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9.1: Balancing Oxidation-Reduction Reactions

Learning Objectives

- Define electrochemistry and a number of important associated terms
- Split oxidation-reduction reactions into their oxidation half-reactions and reduction half-reactions
- Produce balanced oxidation-reduction equations for reactions in acidic or basic solution
- Identify oxidizing agents and reducing agents

Electricity refers to a number of phenomena associated with the presence and flow of electric charge. Electricity includes such diverse things as lightning, static electricity, the current generated by a battery as it discharges, and many other influences on our daily lives. The flow or movement of charge is an electric current (Figure $9.1.1$). Electrons or ions may carry the charge. The elementary unit of charge is the charge of a proton, which is equal in magnitude to the charge of an electron. The SI unit of charge is the coulomb (C) and the charge of a proton is 1.602×10^{-19} C. The presence of an electric charge generates an electric field. Electric current is the rate of flow of charge.

Figure $9.1.1$: Electricity-related phenomena include lightning, accumulation of static electricity, and current produced by a battery. (credit left: modification of work by Thomas Bresson; credit middle: modification of work by Chris Darling; credit right: modification of work by Windell Oskay).

The SI unit for electrical current is the SI base unit called the ampere (A), which is a flow rate of 1 coulomb of charge per second (1 A = 1 C/s). An electric current flows in a path, called an electric circuit. In most chemical systems, it is necessary to maintain a closed path for current to flow. The flow of charge is generated by an electrical potential difference, or potential, between two points in the circuit. Electrical potential is the ability of the electric field to do work on the charge. The SI unit of electrical potential is the volt (V). When 1 coulomb of charge moves through a potential difference of 1 volt, it gains or loses 1 joule (J) of energy. Table $9.1.1$ summarizes some of this information about electricity.

Table $9.1.1$: Common Electrical Terms

Quantity	Definition	Measure or Unit
Electric charge	Charge on a proton	1.602×10^{-19} C
Electric current	The movement of charge	ampere = A = 1 C/s
Electric potential	The force trying to move the charge	volt = V = J/C
Electric field	The force acting upon other charges in the vicinity	

Electrochemistry studies oxidation-reduction reactions, which were first discussed in an earlier chapter, where we learned that oxidation was the loss of electrons and reduction was the gain of electrons. The reactions discussed tended to be rather simple, and conservation of mass (atom counting by type) and deriving a correctly balanced chemical equation were relatively simple. In this section, we will concentrate on the half-reaction method for balancing oxidation-reduction reactions. The use of half-reactions is important partly for balancing more complicated reactions and partly because many aspects of electrochemistry are easier to discuss in terms of half-reactions. There are alternate methods of balancing these reactions; however, there are no good alternatives to half-reactions for discussing what is occurring in many systems. The half-reaction method splits oxidation-reduction reactions into their oxidation "half" and reduction "half" to make finding the overall equation easier.

Electrochemical reactions frequently occur in solutions, which could be acidic, basic, or neutral. When balancing oxidation-reduction reactions, the nature of the solution may be important. It helps to see this in an actual problem. Consider the following unbalanced oxidation-reduction reaction in acidic solution:

$$\mathrm{MnO_4^-}(aq) + \mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + \mathrm{Fe^{3+}}(aq)$$

We can start by collecting the species we have so far into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction. Each of these half-reactions contain the same element in two different oxidation states. The Fe^{2+} has lost an electron to become Fe^{3+}; therefore, the iron underwent oxidation. The reduction is not as obvious; however, the manganese gained five electrons to change from Mn^{7+} to Mn^{2+}.

$$\begin{aligned}\text{oxidation (unbalanced): } & \mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Fe^{3+}}(aq)\\ \text{reduction (unbalanced): } & \mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq)\end{aligned}$$

In acidic solution, there are hydrogen ions present, which are often useful in balancing half-reactions. It may be necessary to use the hydrogen ions directly or as a reactant that may react with oxygen to generate water. Hydrogen ions are very important in acidic solutions where the reactants or products contain hydrogen and/or oxygen. In this example, the oxidation half-reaction involves neither hydrogen nor oxygen, so hydrogen ions are not necessary to the balancing. However, the reduction half-reaction does involve oxygen. It is necessary to use hydrogen ions to convert this oxygen to water.

$$\text{charge not balanced: } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

The situation is different in basic solution because the hydrogen ion concentration is lower and the hydroxide ion concentration is higher. After finishing this example, we will examine how basic solutions differ from acidic solutions. A neutral solution may be treated as acidic or basic, though treating it as acidic is usually easier.

The iron atoms in the oxidation half-reaction are balanced (mass balance); however, the charge is unbalanced, since the charges on the ions are not equal. It is necessary to use electrons to balance the charge. The way to balance the charge is by *adding* electrons to one side of the equation. Adding a single electron on the right side gives a balanced oxidation half-reaction:

$$\text{oxidation (balanced): } \mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Fe^{3+}}(aq) + \mathrm{e^-}$$

You should check the half-reaction for the number of each atom type and the total charge on each side of the equation. The charges include the actual charges of the ions times the number of ions and the charge on an electron times the number of electrons.

$$\begin{aligned}&\text{Fe: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\ &\text{Charge: Does } [1 \times (+2)] = [1 \times (+3) + 1 \times (-1)]\text{? Yes.}\end{aligned}$$

If the atoms and charges balance, the half-reaction is balanced. In oxidation half-reactions, electrons appear as products (on the right). As discussed in the earlier chapter, since iron underwent oxidation, iron is the reducing agent.

Now return to the reduction half-reaction equation:

$$\text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

The atoms are balanced (mass balance), so it is now necessary to check for charge balance. The total charge on the left of the reaction arrow is [(−1) × (1) + (8) × (+1)], or +7, while the total charge on the right side is [(1) × (+2) + (4) × (0)], or +2. The difference between +7 and +2 is five; therefore, it is necessary to add five electrons to the left side to achieve charge balance.

$$\text{Reduction (balanced): } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

You should check this half-reaction for each atom type and for the charge, as well:

$$\begin{aligned}&\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\ &\text{H: Does } (8 \times 1) = (4 \times 2)\text{? Yes.}\\ &\text{O: Does } (1 \times 4) = (4 \times 1)\text{? Yes.}\\ &\text{Charge: Does } [1 \times (-1) + 8 \times (+1) + 5 \times (-1)] = [1 \times (+2)]\text{? Yes.}\end{aligned}$$

Now that this half-reaction is balanced, it is easy to see it involves reduction because electrons were gained when MnO_4^- was reduced to Mn^{2+}. In all reduction half-reactions, electrons appear as reactants (on the left side). As discussed in the earlier chapter, the species that was reduced, MnO_4^- in this case, is also called the oxidizing agent. We now have two balanced half-reactions.

$$\begin{aligned}\text{oxidation: } & \mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Fe^{3+}}(aq) + \mathrm{e^-}\\ \text{reduction: } & \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)\end{aligned}$$

It is now necessary to combine the two halves to produce a whole reaction. The key to combining the half-reactions is the electrons. The electrons lost during oxidation must go somewhere. These electrons go to cause reduction. The number of electrons transferred from the oxidation half-reaction to the reduction half-reaction must be equal. There can be no missing or excess electrons. In this example, the oxidation half-reaction generates one electron, while the reduction half-reaction requires five. The lowest common multiple of one and five is five; therefore, it is necessary to multiply every term in the oxidation half-reaction by five and every term in the reduction half-reaction by one. (In this case, the multiplication of the reduction half-reaction generates no change; however, this will not always be the case.) The multiplication of the two half-reactions by the appropriate factor followed by addition of the two halves gives

$$\begin{array}{l} \text{oxidation: } 5\times(\mathrm{Fe^{2+}}(aq)\longrightarrow \mathrm{Fe^{3+}}(aq)+\mathrm{e^-}) \\ \underline{\text{reduction: } \mathrm{MnO_4^-}(aq)+8\,\mathrm{H^+}(aq)+5\,\mathrm{e^-}\longrightarrow \mathrm{Mn^{2+}}(aq)+4\,\mathrm{H_2O}(l)} \\ \text{overall: } 5\,\mathrm{Fe^{2+}}(aq)+\mathrm{MnO_4^-}(aq)+8\,\mathrm{H^+}(aq)\longrightarrow 5\,\mathrm{Fe^{3+}}(aq)+\mathrm{Mn^{2+}}(aq)+4\,\mathrm{H_2O}(l) \end{array}$$

The electrons do not appear in the final answer because the oxidation electrons are the same electrons as the reduction electrons and they “cancel.” Carefully check each side of the overall equation to verify everything was combined correctly:

$$\begin{array}{l} \text{Fe: Does } (5\times1)=(5\times1)\text{? Yes.} \\ \text{Mn: Does } (1\times1)=(1\times1)\text{? Yes.} \\ \text{H: Does } (8\times1)=(4\times2)\text{? Yes.} \\ \text{O: Does } (1\times4)=(4\times1)\text{? Yes.} \\ \text{Charge: Does } [5\times(+2)+1\times(-1)+8\times(+1)]=[5\times(+3)+1\times(+2)]\text{? Yes.} \end{array}$$

Everything checks, so this is the overall equation in acidic solution. If something does not check, the most common error occurs during the multiplication of the individual half-reactions.

Now suppose we wanted the solution to be basic. Recall that basic solutions have excess hydroxide ions. Some of these hydroxide ions will react with hydrogen ions to produce water. The simplest way to generate the balanced overall equation in basic solution is to start with the balanced equation in acidic solution, then “convert” it to the equation for basic solution. However, it is necessary to exercise caution when doing this, as many reactants behave differently under basic conditions and many metal ions will precipitate as the metal hydroxide. We just produced the following reaction, which we want to change to a basic reaction:

$$5\,\mathrm{Fe^{2+}}(aq)+\mathrm{MnO_4^-}(aq)+8\,\mathrm{H^+}(aq)\longrightarrow 5\,\mathrm{Fe^{3+}}(aq)+\mathrm{Mn^{2+}}(aq)+4\,\mathrm{H_2O}(l)$$

However, under basic conditions, $\mathrm{MnO_4^-}$ normally reduces to MnO_2 and iron will be present as either $Fe(OH)_2$ or $Fe(OH)_3$. For these reasons, under basic conditions, this reaction will be

$$3\,\mathrm{Fe(OH)_2}(s)+\mathrm{MnO_4^-}(aq)+2\,\mathrm{H_2O}(l)\longrightarrow 3\,\mathrm{Fe(OH)_3}(s)+\mathrm{MnO_2}(s)+\mathrm{OH^-}(aq)$$

(Under very basic conditions $\mathrm{MnO_4^-}$ will reduce to $\mathrm{MnO_4^{2-}}$, instead of MnO_2.)

It is still possible to balance any oxidation-reduction reaction as an acidic reaction and then, when necessary, convert the equation to a basic reaction. This will work if the acidic and basic reactants and products are the same or if the basic reactants and products are used before the conversion from acidic or basic. There are very few examples in which the acidic and basic reactions will involve the same reactants and products. However, balancing a basic reaction as acidic and then converting to basic will work. To convert to a basic reaction, it is necessary to add the same number of hydroxide ions to each side of the equation so that all the hydrogen ions (H^+) are removed and mass balance is maintained. Hydrogen ion combines with hydroxide ion (OH^-) to produce water.

Let us now try a basic equation. We will start with the following basic reaction:

$$\mathrm{Cl^-}(aq)+\mathrm{MnO_4^-}(aq)\longrightarrow \mathrm{ClO_3^-}(aq)+\mathrm{MnO_2}(s)$$

Balancing this as acid gives

$$\mathrm{Cl^-}(aq)+2\,\mathrm{MnO_4^-}(aq)+2\,\mathrm{H^+}(aq)\longrightarrow \mathrm{ClO_3^-}(aq)+2\,\mathrm{MnO_2}(s)+\mathrm{H_2O}(l)$$

In this case, it is necessary to add two hydroxide ions to each side of the equation to convert the two hydrogen ions on the left into water:

$$\mathrm{Cl^-}(aq)+2\,\mathrm{MnO_4^-}(aq)+(2\,\mathrm{H^+}+2\,\mathrm{OH^-})(aq)\longrightarrow \mathrm{ClO_3^-}(aq)+2\,\mathrm{MnO_2}(s)+\mathrm{H_2O}(l)+2\,\mathrm{OH^-}(aq)$$

$$Cl^-(aq) + 2\,MnO_4^-(aq) + (2\,H_2O)(l) \longrightarrow ClO_3^-(aq) + 2\,MnO_2(s) + H_2O(l) + 2\,OH^-(aq)$$

Note that both sides of the equation show water. Simplifying should be done when necessary, and gives the desired equation. In this case, it is necessary to remove one H_2O from each side of the reaction arrows.

$$Cl^-(aq) + 2\,MnO_4^-(aq) + H_2O(l) \longrightarrow ClO_3^-(aq) + 2\,MnO_2(s) + 2\,OH^-(aq)$$

Again, check each side of the overall equation to make sure there are no errors:

$$\begin{array}{l} \text{Cl: Does } (1 \times 1) = (1 \times 1)\text{? Yes.} \\ \text{Mn: Does } (2 \times 1) = (2 \times 1)\text{? Yes.} \\ \text{H: Does } (1 \times 2) = (2 \times 1)\text{? Yes.} \\ \text{O: Does } (2 \times 4 + 1 \times 1) = (3 \times 1 + 2 \times 2 + 2 \times 1)\text{? Yes.} \\ \text{Charge: Does } [1 \times (-1) + 2 \times (-1)] = [1 \times (-1) + 2 \times (-1)]\text{? Yes.} \end{array}$$

Everything checks, so this is the overall equation in basic solution.

✓ Example 9.1.1: Balancing Acidic Oxidation-Reduction Reactions

Balance the following reaction equation in acidic solution:

$$MnO_4^-(aq) + Cr^{3+}(aq) \longrightarrow Mn^{2+}(aq) + Cr_2O_7^{2-}(aq)$$

Solution

This is an oxidation-reduction reaction, so start by collecting the species given into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction.

$$\begin{array}{l} \text{oxidation (unbalanced): } Cr^{3+}(aq) \longrightarrow Cr_2O_7^{2-}(aq) \\ \text{reduction (unbalanced): } MnO_4^-(aq) \longrightarrow Mn^{2+}(aq) \end{array}$$

Starting with the oxidation half-reaction, we can balance the chromium

$$\text{oxidation (unbalanced): } 2\,Cr^{3+}(aq) \longrightarrow Cr_2O_7^{2-}(aq)$$

In acidic solution, we can use or generate hydrogen ions (H^+). Adding seven water molecules to the left side provides the necessary oxygen; the “left over” hydrogen appears as 14 H^+ on the right:

$$\text{oxidation (unbalanced): } 2\,Cr^{3+}(aq) + 7\,H_2O(l) \longrightarrow Cr_2O_7^{2-}(aq) + 14\,H^+(aq)$$

The left side of the equation has a total charge of [2 × (+3) = +6], and the right side a total charge of [−2 + 14 × (+1) = +12]. The difference is six; adding six electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):

$$\text{oxidation (balanced): } 2\,Cr^{3+}(aq) + 7\,H_2O(l) \longrightarrow Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^-$$

Checking the half-reaction:

$$\begin{array}{l} \text{Cr: Does } (2 \times 1) = (1 \times 2)\text{? Yes.} \\ \text{H: Does } (7 \times 2) = (14 \times 1)\text{? Yes.} \\ \text{O: Does } (7 \times 1) = (1 \times 7)\text{? Yes.} \\ \text{Charge: Does } [2 \times (+3)] = [1 \times (-2) + 14 \times (+1) + 6 \times (-1)]\text{? Yes.} \end{array}$$

Now work on the reduction. It is necessary to convert the four oxygen atoms in the permanganate into four water molecules. To do this, add eight H^+ to convert the oxygen into four water molecules:

$$\text{reduction (unbalanced): } MnO_4^-(aq) + 8\,H^+(aq) \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

Then add five electrons to the left side to balance the charge:

$$\text{reduction (balanced): } MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

Make sure to check the half-reaction:

$$\begin{aligned}&\text{Mn: Does } (1\times 1)=(1\times 1)\text{? Yes.}\\&\text{H: Does } (8\times 1)=(4\times 2)\text{? Yes.}\\&\text{O: Does } (1\times 4)=(4\times 1)\text{? Yes.}\\&\text{Charge: Does } [1\times(-1)+8\times(+1)+5\times(-1)]=[1\times(+2)]\text{? Yes.}\end{aligned}$$

Collecting what we have so far:

$$\begin{aligned}&\text{oxidation: } 2\,Cr^{3+}(aq)+7\,H_2O(l)\longrightarrow Cr_2O_7^{2-}(aq)+14\,H^+(aq)+6\,e^-\\&\text{reduction: } MnO_4^-(aq)+8\,H^+(aq)+5\,e^-\longrightarrow Mn^{2+}(aq)+4\,H_2O(l)\end{aligned}$$

The least common multiple for the electrons is 30, so multiply the oxidation half-reaction by five, the reduction half-reaction by six, combine, and simplify:

$$10\,Cr^{3+}(aq)+35\,H_2O(l)+6\,MnO_4^-(aq)+48\,H^+(aq)\longrightarrow 5\,Cr_2O_7^{2-}(aq)+70\,H^+(aq)+6\,Mn^{2+}(aq)+24\,H_2O(l)$$

$$10\,Cr^{3+}(aq)+11\,H_2O(l)+6\,MnO_4^-(aq)\longrightarrow 5\,Cr_2O_7^{2-}(aq)+22\,H^+(aq)+6\,Mn^{2+}(aq)$$

Checking each side of the equation:

$$\begin{aligned}&\text{Mn: Does } (6\times 1)=(6\times 1)\text{? Yes.}\\&\text{Cr: Does } (10\times 1)=(5\times 2)\text{? Yes.}\\&\text{H: Does } (11\times 2)=(22\times 1)\text{? Yes.}\\&\text{O: Does } (11\times 1+6\times 4)=(5\times 7)\text{? Yes.}\\&\text{Charge: Does } [10\times(+3)+6\times(-1)]=[5\times(-2)+22\times(+1)+6\times(+2)]\text{? Yes.}\end{aligned}$$

This is the balanced equation in acidic solution.

? Exercise 9.1.1

Balance the following equation in acidic solution:

$$Hg_2^{2+}+Ag\longrightarrow Hg+Ag^+$$

Answer

$$Hg_2^{2+}(aq)+2\,Ag(s)\longrightarrow 2\,Hg(l)+2\,Ag^+(aq)$$

✓ Example 9.1.2: Balancing Basic Oxidation-Reduction Reactions

Balance the following reaction equation in basic solution:

$$MnO_4^-(aq)+Cr(OH)_3(s)\longrightarrow MnO_2(s)+CrO_4^{2-}(aq)$$

Solution

This is an oxidation-reduction reaction, so start by collecting the species given into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction

$$\begin{aligned}&\text{oxidation (unbalanced): } Cr(OH)_3(s)\longrightarrow CrO_4^{2-}(aq)\\&\text{reduction (unbalanced): } MnO_4^-(aq)\longrightarrow MnO_2(s)\end{aligned}$$

Starting with the oxidation half-reaction, we can balance the chromium

$$\text{oxidation (unbalanced): } Cr(OH)_3(s)\longrightarrow CrO_4^{2-}(aq)$$

In acidic solution, we can use or generate hydrogen ions (H^+). Adding one water molecule to the left side provides the necessary oxygen; the “left over” hydrogen appears as five H^+ on the right side:

$$\text{oxidation (unbalanced): } Cr(OH)_3(s)+H_2O(l)\longrightarrow CrO_4^{2-}(aq)+5\,H^+(aq)$$

The left side of the equation has a total charge of [0], and the right side a total charge of [−2 + 5 × (+1) = +3]. The difference is three, adding three electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):

$$\text{oxidation (balanced): } \mathrm{Cr(OH)_3}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{CrO_4^{2-}}(aq) + 5\,\mathrm{H^+}(aq) + 3\,\mathrm{e^-}$$

Checking the half-reaction:

$$\begin{aligned} &\text{Cr: Does } (1 \times 1) = (1 \times 1)\text{? Yes.} \\ &\text{H: Does } (1 \times 3 + 1 \times 2) = (5 \times 1)\text{? Yes.} \\ &\text{O: Does } (1 \times 3 + 1 \times 1) = (4 \times 1)\text{? Yes.} \\ &\text{Charge: Does } [0 = [1 \times (-2) + 5 \times (+1) + 3 \times (-1)]\text{? Yes.} \end{aligned}$$

Now work on the reduction. It is necessary to convert the four O atoms in the MnO_4^- minus the two O atoms in MnO_2 into two water molecules. To do this, add four H^+ to convert the oxygen into two water molecules:

$$\text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) + 4\,\mathrm{H^+}(aq) \longrightarrow \mathrm{MnO_2}(s) + 2\,\mathrm{H_2O}(l)$$

Then add three electrons to the left side to balance the charge:

$$\text{reduction (balanced): } \mathrm{MnO_4^-}(aq) + 4\,\mathrm{H^+}(aq) + 3\,\mathrm{e^-} \longrightarrow \mathrm{MnO_2}(s) + 2\,\mathrm{H_2O}(l)$$

Make sure to check the half-reaction:

$$\begin{aligned} &\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.} \\ &\text{H: Does } (4 \times 1) = (2 \times 2)\text{? Yes.} \\ &\text{O: Does } (1 \times 4) = (1 \times 2 + 2 \times 1)\text{? Yes.} \\ &\text{Charge: Does } [1 \times (-1) + 4 \times (+1) + 3 \times (-1)] = [0]\text{? Yes.} \end{aligned}$$

Collecting what we have so far:

$$\begin{aligned} &\text{oxidation: } \mathrm{Cr(OH)_3}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{CrO_4^{2-}}(aq) + 5\,\mathrm{H^+}(aq) + 3\,\mathrm{e^-} \\ &\text{reduction: } \mathrm{MnO_4^-}(aq) + 4\,\mathrm{H^+}(aq) + 3\,\mathrm{e^-} \longrightarrow \mathrm{MnO_2}(s) + 2\,\mathrm{H_2O}(l) \end{aligned}$$

In this case, both half reactions involve the same number of electrons; therefore, simply add the two half-reactions together.

$$\mathrm{MnO_4^-}(aq) + 4\,\mathrm{H^+}(aq) + \mathrm{Cr(OH)_3}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{CrO_4^{2-}}(aq) + \mathrm{MnO_2}(s) + 2\,\mathrm{H_2O}(l) + 5\,\mathrm{H^+}(aq)$$

$$\mathrm{MnO_4^-}(aq) + \mathrm{Cr(OH)_3}(s) \longrightarrow \mathrm{CrO_4^{2-}}(aq) + \mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + \mathrm{H^+}(aq)$$

Checking each side of the equation:

$$\begin{aligned} &\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.} \\ &\text{Cr: Does } (1 \times 1) = (1 \times 1)\text{? Yes.} \\ &\text{H: Does } (1 \times 3) = (2 \times 1 + 1 \times 1)\text{? Yes.} \\ &\text{O: Does } (1 \times 4 + 1 \times 3) = (1 \times 4 + 1 \times 2 + 1 \times 1)\text{? Yes.} \\ &\text{Charge: Does } [1 \times (-1)] = [1 \times (-2) + 1 \times (+1)]\text{? Yes.} \end{aligned}$$

This is the balanced equation in acidic solution. For a basic solution, add one hydroxide ion to each side and simplify:

$$\mathrm{OH^-}(aq) + \mathrm{MnO_4^-}(aq) + \mathrm{Cr(OH)_3}(s) \longrightarrow \mathrm{CrO_4^{2-}}(aq) + \mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + (\mathrm{H^+} + \mathrm{OH^-})(aq)$$

$$\mathrm{OH^-}(aq) + \mathrm{MnO_4^-}(aq) + \mathrm{Cr(OH)_3}(s) \longrightarrow \mathrm{CrO_4^{2-}}(aq) + \mathrm{MnO_2}(s) + 2\,\mathrm{H_2O}(l)$$

Checking each side of the equation:

$$\begin{aligned} &\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.} \\ &\text{Cr: Does } (1 \times 1) = (1 \times 1)\text{? Yes.} \\ &\text{H: Does } (1 \times 1 + 1 \times 3) = (2 \times 2)\text{? Yes.} \\ &\text{O: Does } (1 \times 1 + 1 \times 4 + 1 \times 3) = (1 \times 4 + 1 \times 2 + 2 \times 1)\text{? Yes.} \\ &\text{Charge: Does } [1 \times (-1) + 1 \times (-1)] = [1 \times (-2)]\text{? Yes.} \end{aligned}$$

This is the balanced equation in basic solution.

Exercise 9.1.2

Balance the following in the type of solution indicated.

a. $H_2 + Cu^{2+} \longrightarrow Cu \quad \text{(acidic solution)}$
b. $H_2 + Cu(OH)_2 \longrightarrow Cu \quad \text{(basic solution)}$
c. $Fe + Ag^{+} \longrightarrow Fe^{2+} + Ag$
d. Identify the oxidizing agents in reactions (a), (b), and (c).
e. Identify the reducing agents in reactions (a), (b), and (c).

Answer a

$$H_2(g) + Cu^{2+}(aq) \longrightarrow 2\,H^{+}(aq) + Cu(s)$$

Answer b

$$H_2(g) + Cu(OH)_2(s) \longrightarrow 2\,H_2O(l) + Cu(s)$$

Answer c

$$Fe(s) + 2\,Ag^{+}(aq) \longrightarrow Fe^{2+}(aq) + 2\,Ag(s)$$

Answer d

oxidizing agent = species reduced: Cu^{2+}, $Cu(OH)_2$, Ag^{+}

Answer e

reducing agent = species oxidized: H_2, H_2, Fe.

Summary

An electric current consists of moving charge. The charge may be in the form of electrons or ions. Current flows through an unbroken or closed circular path called a circuit. The current flows through a conducting medium as a result of a difference in electrical potential between two points in a circuit. Electrical potential has the units of energy per charge. In SI units, charge is measured in coulombs (C), current in amperes $\left(A = \frac{C}{s}\right)$, and electrical potential in volts $\left(V = \frac{J}{C}\right)$.

Oxidation is the loss of electrons, and the species that is oxidized is also called the reducing agent. Reduction is the gain of electrons, and the species that is reduced is also called the oxidizing agent. Oxidation-reduction reactions can be balanced using the half-reaction method. In this method, the oxidation-reduction reaction is split into an oxidation half-reaction and a reduction half-reaction. The oxidation half-reaction and reduction half-reaction are then balanced separately. Each of the half-reactions must have the same number of each type of atom on both sides of the equation *and* show the same total charge on each side of the equation. Charge is balanced in oxidation half-reactions by adding electrons as products; in reduction half-reactions, charge is balanced by adding electrons as reactants. The total number of electrons gained by reduction must exactly equal the number of electrons lost by oxidation when combining the two half-reactions to give the overall balanced equation. Balancing oxidation-reduction reaction equations in aqueous solutions frequently requires that oxygen or hydrogen be added or removed from a reactant. In acidic solution, hydrogen is added by adding hydrogen ion (H^{+}) and removed by producing hydrogen ion; oxygen is removed by adding hydrogen ion and producing water, and added by adding water and producing hydrogen ion. A balanced equation in basic solution can be obtained by first balancing the equation in acidic solution, and then adding hydroxide ion to each side of the balanced equation in such numbers that all the hydrogen ions are converted to water.

Glossary

circuit

path taken by a current as it flows because of an electrical potential difference

current

flow of electrical charge; the SI unit of charge is the coulomb (C) and current is measured in amperes $\left(1\ A = 1\ \frac{C}{s}\right)$

electrical potential

energy per charge; in electrochemical systems, it depends on the way the charges are distributed within the system; the SI unit of electrical potential is the volt $\left(1\text{ V} = 1\,\frac{\text{J}}{\text{C}}\right)$

half-reaction method

method that produces a balanced overall oxidation-reduction reaction by splitting the reaction into an oxidation "half" and reduction "half," balancing the two half-reactions, and then combining the oxidation half-reaction and reduction half-reaction in such a way that the number of electrons generated by the oxidation is exactly canceled by the number of electrons required by the reduction

oxidation half-reaction

the "half" of an oxidation-reduction reaction involving oxidation; the half-reaction in which electrons appear as products; balanced when each atom type, as well as the charge, is balanced

reduction half-reaction

the "half" of an oxidation-reduction reaction involving reduction; the half-reaction in which electrons appear as reactants; balanced when each atom type, as well as the charge, is balanced

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9.2: Galvanic Cells

Learning Objectives

- Use cell notation to describe galvanic cells
- Describe the basic components of galvanic cells

Galvanic cells, also known as voltaic cells, are electrochemical cells in which spontaneous oxidation-reduction reactions produce electrical energy. In writing the equations, it is often convenient to separate the oxidation-reduction reactions into half-reactions to facilitate balancing the overall equation and to emphasize the actual chemical transformations.

Consider what happens when a clean piece of copper metal is placed in a solution of silver nitrate (Figure 9.2.1). As soon as the copper metal is added, silver metal begins to form and copper ions pass into the solution. The blue color of the solution on the far right indicates the presence of copper ions. The reaction may be split into its two half-reactions. Half-reactions separate the oxidation from the reduction, so each can be considered individually.

$$\text{oxidation: } \mathrm{Cu}(s) \longrightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{e^-} \tag{9.2.1}$$

$$\text{reduction: } 2 \times (\mathrm{Ag^+}(aq) + \mathrm{e^-} \longrightarrow \mathrm{Ag}(s)) \quad \text{or} \quad 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}(s) \tag{9.2.2}$$

$$\text{overall: } 2\,\mathrm{Ag^+}(aq) + \mathrm{Cu}(s) \longrightarrow 2\,\mathrm{Ag}(s) + \mathrm{Cu^{2+}}(aq) \tag{9.2.3}$$

The equation for the reduction half-reaction had to be doubled so the number electrons “gained” in the reduction half-reaction equaled the number of electrons “lost” in the oxidation half-reaction.

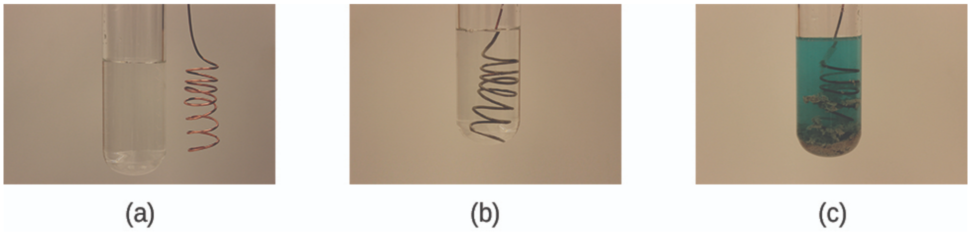

Figure 9.2.1: When a clean piece of copper metal is placed into a clear solution of silver nitrate (a), an oxidation-reduction reaction occurs that results in the exchange of $\mathrm{Cu^{2+}}$ for $\mathrm{Ag^+}$ ions in solution. As the reaction proceeds (b), the solution turns blue (c) because of the copper ions present, and silver metal is deposited on the copper strip as the silver ions are removed from solution. (credit: modification of work by Mark Ott)

Galvanic or voltaic cells involve spontaneous electrochemical reactions in which the half-reactions are separated (Figure 9.2.2) so that current can flow through an external wire. The beaker on the left side of the figure is called a half-cell, and contains a 1 *M* solution of copper(II) nitrate [$\mathrm{Cu(NO_3)_2}$] with a piece of copper metal partially submerged in the solution. The copper metal is an electrode. The copper is undergoing oxidation; therefore, the copper electrode is the anode. The anode is connected to a voltmeter with a wire and the other terminal of the voltmeter is connected to a silver electrode by a wire. The silver is undergoing reduction; therefore, the silver electrode is the cathode. The half-cell on the right side of the figure consists of the silver electrode in a 1 *M* solution of silver nitrate ($\mathrm{AgNO_3}$). At this point, no current flows—that is, no significant movement of electrons through the wire occurs because the circuit is open. The circuit is closed using a salt bridge, which transmits the current with moving ions. The salt bridge consists of a concentrated, nonreactive, electrolyte solution such as the sodium nitrate ($\mathrm{NaNO_3}$) solution used in this example. As electrons flow from left to right through the electrode and wire, nitrate ions (anions) pass through the porous plug on the left into the copper(II) nitrate solution. This keeps the beaker on the left electrically neutral by neutralizing the charge on the copper(II) ions that are produced in the solution as the copper metal is oxidized. At the same time, the nitrate ions are moving to the left, sodium ions (cations) move to the right, through the porous plug, and into the silver nitrate solution on the right. These added cations “replace” the silver ions that are removed from the solution as they were reduced to silver metal, keeping the beaker on the right electrically neutral. Without the salt bridge, the compartments would not remain electrically neutral and no significant current would flow. However, if the two compartments are in direct contact, a salt bridge is not necessary. The instant the circuit is completed, the voltmeter reads +0.46 V, this is called the cell potential. The cell potential is created when the two dissimilar metals are connected, and is a measure of the energy per unit charge available from the oxidation-reduction reaction. The volt is the derived SI unit for electrical potential

$$\text{volt} = V = \frac{\text{J}}{\text{C}}$$

In this equation, A is the current in amperes and C the charge in coulombs. Note that volts must be multiplied by the charge in coulombs (C) to obtain the energy in joules (J).

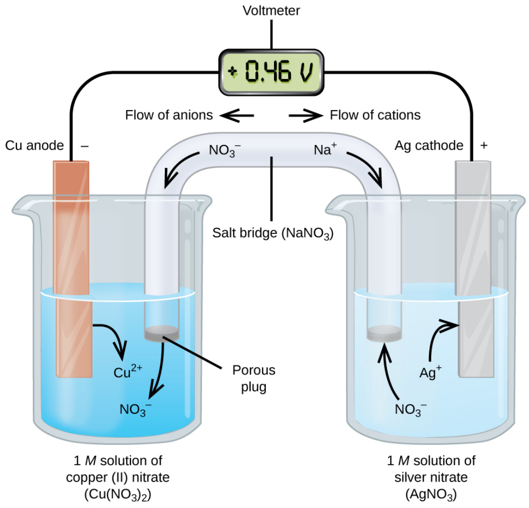

Figure 9.2.2: In this standard galvanic cell, the half-cells are separated; electrons can flow through an external wire and become available to do electrical work.

When the electrochemical cell is constructed in this fashion, a positive cell potential indicates a spontaneous reaction *and* that the electrons are flowing from the left to the right. There is a lot going on in Figure 9.2.2, so it is useful to summarize things for this system:

- Electrons flow from the anode to the cathode: left to right in the standard galvanic cell in the figure.
- The electrode in the left half-cell is the anode because oxidation occurs here. The name refers to the flow of anions in the salt bridge toward it.
- The electrode in the right half-cell is the cathode because reduction occurs here. The name refers to the flow of cations in the salt bridge toward it.
- Oxidation occurs at the anode (the left half-cell in the figure).
- Reduction occurs at the cathode (the right half-cell in the figure).
- The cell potential, +0.46 V, in this case, results from the inherent differences in the nature of the materials used to make the two half-cells.
- The salt bridge must be present to close (complete) the circuit and both an oxidation and reduction must occur for current to flow.

There are many possible galvanic cells, so a shorthand notation is usually used to describe them. The cell notation (sometimes called a cell diagram) provides information about the various species involved in the reaction. This notation also works for other types of cells. A vertical line, $|$, denotes a phase boundary and a double line, $\|$, the salt bridge. Information about the anode is written to the left, followed by the anode solution, then the salt bridge (when present), then the cathode solution, and, finally, information about the cathode to the right. The cell notation for the galvanic cell in Figure 9.2.2 is then

$$\text{Cu}(s)\,|\,\text{Cu}^{2+}(aq,\ 1\ M)\,\|\,\text{Ag}^{+}(aq,\ 1\ M)\,|\,\text{Ag}(s)$$

Note that spectator ions are not included and that the simplest form of each half-reaction was used. When known, the initial concentrations of the various ions are usually included.

One of the simplest cells is the Daniell cell. It is possible to construct this battery by placing a copper electrode at the bottom of a jar and covering the metal with a copper sulfate solution. A zinc sulfate solution is floated on top of the copper sulfate solution; then a zinc electrode is placed in the zinc sulfate solution. Connecting the copper electrode to the zinc electrode allows an electric current to flow. This is an example of a cell without a salt bridge, and ions may flow across the interface between the two solutions.

Some oxidation-reduction reactions involve species that are poor conductors of electricity, and so an electrode is used that does not participate in the reactions. Frequently, the electrode is platinum, gold, or graphite, all of which are inert to many chemical reactions. One such system is shown in Figure 9.2.3. Magnesium undergoes oxidation at the anode on the left in the figure and hydrogen ions undergo reduction at the cathode on the right. The reaction may be summarized as

$$\text{oxidation: } \mathrm{Mg}(s) \longrightarrow \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{e^-} \tag{9.2.4}$$

$$\text{reduction: } 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}(g) \tag{9.2.5}$$

$$\text{overall: } \mathrm{Mg}(s) + 2\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Mg^{2+}}(aq) + \mathrm{H_2}(g) \tag{9.2.6}$$

The cell used an inert platinum wire for the cathode, so the cell notation is

$$\mathrm{Mg}(s)\,|\,\mathrm{Mg^{2+}}(aq)\,\|\,\mathrm{H^+}(aq)\,|\,\mathrm{H_2}(g)\,|\,\mathrm{Pt}(s)$$

The magnesium electrode is an active electrode because it participates in the oxidation-reduction reaction. Inert electrodes, like the platinum electrode in Figure 9.2.3, do not participate in the oxidation-reduction reaction and are present so that current can flow through the cell. Platinum or gold generally make good inert electrodes because they are chemically unreactive.

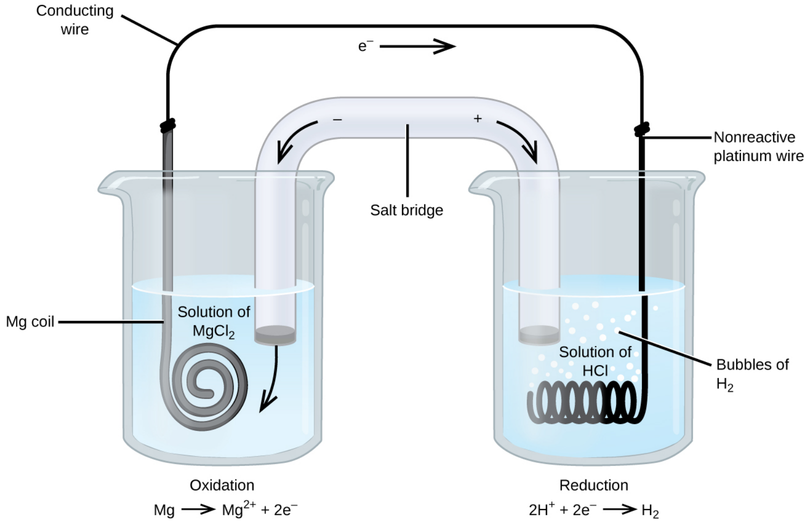

Figure 9.2.2: The oxidation of magnesium to magnesium ion occurs in the beaker on the left side in this apparatus; the reduction of hydrogen ions to hydrogen occurs in the beaker on the right. A nonreactive, or inert, platinum wire allows electrons from the left beaker to move into the right beaker. The overall reaction is: $\mathrm{Mg} + 2\,\mathrm{H^+} \longrightarrow \mathrm{Mg^{2+}} + \mathrm{H_2}$, *which is represented in cell notation as:* $\mathrm{Mg}(s)\,|\,\mathrm{Mg^{2+}}(aq)\,\|\,\mathrm{H^+}(aq)\,|\,\mathrm{H_2}(g)\,|\,\mathrm{Pt}(s)$

✓ Example 9.2.1: Using Cell Notation

Consider a galvanic cell consisting of

$$2\,\mathrm{Cr}(s) + 3\,\mathrm{Cu^{2+}}(aq) \longrightarrow 2\,\mathrm{Cr^{3+}}(aq) + 3\,\mathrm{Cu}(s)$$

Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Cr is oxidized when three electrons are lost to form Cr^{3+}, and Cu^{2+} is reduced as it gains two electrons to form Cu. Balancing the charge gives

$$\text{oxidation: } 2\,\mathrm{Cr}(s) \longrightarrow 2\,\mathrm{Cr^{3+}}(aq) + 6\,\mathrm{e^-} \tag{9.2.7}$$

$$\text{reduction: } 3\,\mathrm{Cu^{2+}}(aq) + 6\,\mathrm{e^-} \longrightarrow 3\,\mathrm{Cu}(s) \tag{9.2.8}$$

$$\text{overall: } 2\,\mathrm{Cr}(s) + 3\,\mathrm{Cu^{2+}}(aq) \longrightarrow 2\,\mathrm{Cr^{3+}}(aq) + 3\,\mathrm{Cu}(s) \tag{9.2.9}$$

Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. No concentrations were specified so:

$$\mathrm{Cr}(s)\,|\,\mathrm{Cr^{3+}}(aq)\,\|\,\mathrm{Cu^{2+}}(aq)\,|\,\mathrm{Cu}(s).$$

Oxidation occurs at the anode and reduction at the cathode.

✓ Example 9.2.2: Using Cell Notation

Consider a galvanic cell consisting of

$$5\,Fe^{2+}(aq) + MnO_4^-(aq) + 8\,H^+(aq) \longrightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$$

Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Fe^{2+} undergoes oxidation when one electron is lost to form Fe^{3+}, and MnO_4^- is reduced as it gains five electrons to form Mn^{2+}. Balancing the charge gives

$$\text{oxidation: } 5(Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-) \tag{9.2.10}$$

$$\underline{\text{reduction: } MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)} \tag{9.2.11}$$

$$\text{overall: } 5\,Fe^{2+}(aq) + MnO_4^-(aq) + 8\,H^+(aq) \longrightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l) \tag{9.2.12}$$

Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. It is necessary to use an inert electrode, such as platinum, because there is no metal present to conduct the electrons from the anode to the cathode. No concentrations were specified so:

$$Pt(s)\,|\,Fe^{2+}(aq),\ Fe^{3+}(aq)\,\|\,MnO_4^-(aq),\ H^+(aq),\ Mn^{2+}(aq)\,|\,Pt(s).$$

Oxidation occurs at the anode and reduction at the cathode.

? Exercise 9.2.1

Use cell notation to describe the galvanic cell where copper(II) ions are reduced to copper metal and zinc metal is oxidized to zinc ions.

Answer

From the information given in the problem:

$$\text{anode (oxidation): } Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^- \tag{9.2.13}$$

$$\underline{\text{cathode (reduction): } Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)} \tag{9.2.14}$$

$$\text{overall: } Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \tag{9.2.15}$$

Using cell notation:

$$Zn(s)\,|\,Zn^{2+}(aq)\,\|\,Cu^{2+}(aq)\,|\,Cu(s).$$

Summary

Electrochemical cells typically consist of two half-cells. The half-cells separate the oxidation half-reaction from the reduction half-reaction and make it possible for current to flow through an external wire. One half-cell, normally depicted on the left side in a figure, contains the anode. Oxidation occurs at the anode. The anode is connected to the cathode in the other half-cell, often shown on the right side in a figure. Reduction occurs at the cathode. Adding a salt bridge completes the circuit allowing current to flow. Anions in the salt bridge flow toward the anode and cations in the salt bridge flow toward the cathode. The movement of these ions completes the circuit and keeps each half-cell electrically neutral. Electrochemical cells can be described using cell notation. In this notation, information about the reaction at the anode appears on the left and information about the reaction at the cathode on the right. The salt bridge is represented by a double line, ‖. The solid, liquid, or aqueous phases within a half-cell are separated by a single line, │. The phase and concentration of the various species is included after the species name. Electrodes that participate in the oxidation-reduction reaction are called active electrodes. Electrodes that do not participate in the oxidation-reduction reaction but are there to allow current to flow are inert electrodes. Inert electrodes are often made from platinum or gold, which are unchanged by many chemical reactions.

Glossary

active electrode

electrode that participates in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

anode

electrode in an electrochemical cell at which oxidation occurs; information about the anode is recorded on the left side of the salt bridge in cell notation

cathode

electrode in an electrochemical cell at which reduction occurs; information about the cathode is recorded on the right side of the salt bridge in cell notation

cell notation

shorthand way to represent the reactions in an electrochemical cell

cell potential

difference in electrical potential that arises when dissimilar metals are connected; the driving force for the flow of charge (current) in oxidation-reduction reactions

galvanic cell

electrochemical cell that involves a spontaneous oxidation-reduction reaction; electrochemical cells with positive cell potentials; also called a voltaic cell

inert electrode

electrode that allows current to flow, but that does not otherwise participate in the oxidation-reduction reaction in an electrochemical cell; the mass of an inert electrode does not change during the oxidation-reduction reaction; inert electrodes are often made of platinum or gold because these metals are chemically unreactive.

voltaic cell

another name for a galvanic cell

9.3: Standard Reduction Potentials

Learning Objectives

- Determine standard cell potentials for oxidation-reduction reactions
- Use standard reduction potentials to determine the better oxidizing or reducing agent from among several possible choices

The cell potential results from the difference in the electrical potentials for each electrode. While it is impossible to determine the electrical potential of a single electrode, we can assign an electrode the value of zero and then use it as a reference. The electrode chosen as the zero is shown in Figure 17.4.1 and is called the standard hydrogen electrode (SHE). The SHE consists of 1 atm of hydrogen gas bubbled through a 1 M HCl solution, usually at room temperature. Platinum, which is chemically inert, is used as the electrode. The reduction half-reaction chosen as the reference is

$$2\,\mathrm{H^+}(aq,\ 1\ M) + 2\,\mathrm{e^-} \rightleftharpoons \mathrm{H_2}(g,\ 1\ \mathrm{atm}) \qquad E^\circ = 0\ \mathrm{V}$$

E° is the standard reduction potential. The superscript "°" on the E denotes standard conditions (1 bar or 1 atm for gases, 1 M for solutes). The voltage is defined as zero for all temperatures.

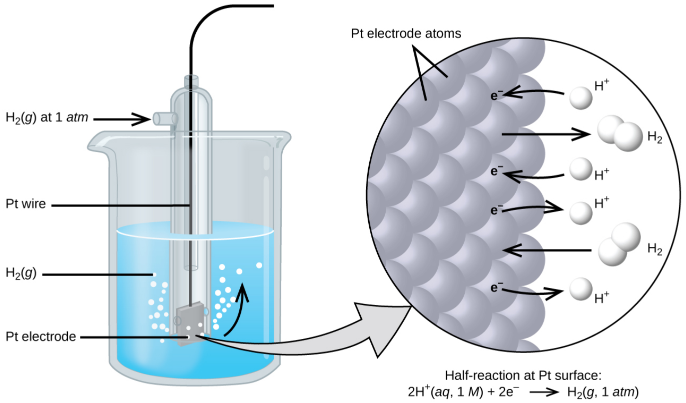

Figure 9.3.1: Hydrogen gas at 1 atm is bubbled through 1 M HCl solution. Platinum, which is inert to the action of the 1 M HCl, is used as the electrode. Electrons on the surface of the electrode combine with H^+ in solution to produce hydrogen gas.

A galvanic cell consisting of a SHE and Cu^{2+}/Cu half-cell can be used to determine the standard reduction potential for Cu^{2+} (Figure 9.3.2). In cell notation, the reaction is

$$\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g,\ 1\ \mathrm{atm})\,|\,\mathrm{H^+}(aq,\ 1\ M)\,\|\,\mathrm{Cu^{2+}}(aq,\ 1\ M)\,|\,\mathrm{Cu}(s)$$

Electrons flow from the anode to the cathode. The reactions, which are reversible, are

$$\begin{array}{l} \text{Anode (oxidation): } \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \\ \text{Cathode (reduction): } \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cu}(s) \\ \hline \text{Overall: } \mathrm{Cu^{2+}}(aq) + \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + \mathrm{Cu}(s) \end{array}$$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is necessary because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$+0.34\ \mathrm{V} = E^\circ_{\mathrm{Cu^{2+}/Cu}} - E^\circ_{\mathrm{H^+/H_2}} = E^\circ_{\mathrm{Cu^{2+}/Cu}} - 0 = E^\circ_{\mathrm{Cu^{2+}/Cu}}$$

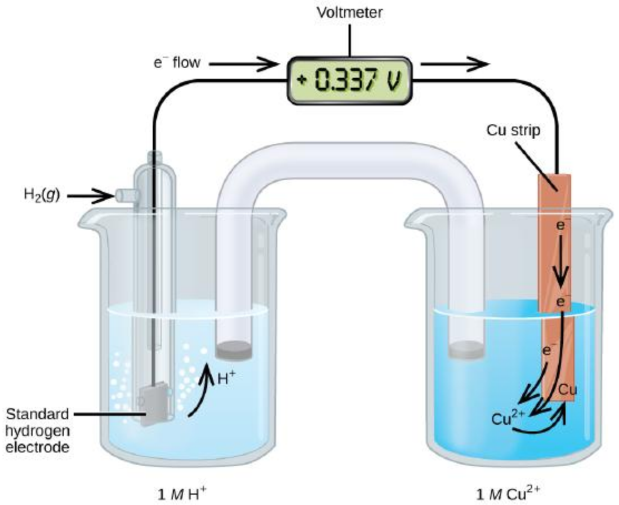

Figure 9.3.2: A galvanic cell can be used to determine the standard reduction potential of Cu^{2+}.

Using the SHE as a reference, other standard reduction potentials can be determined. Consider the cell shown in Figure 9.3.2, where

$$\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g,\ 1\ \mathrm{atm})\,|\,\mathrm{H^+}(aq,\ 1\ M)\,\|\,\mathrm{Ag^+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s)$$

Electrons flow from left to right, and the reactions are

$$\begin{array}{l}\text{anode (oxidation): } \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \\ \text{cathode (reduction): } 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}(s) \\ \hline \text{overall: } 2\,\mathrm{Ag^+}(aq) + \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{Ag}(s)\end{array}$$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is needed because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$+0.80\ \mathrm{V} = E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{H^+/H_2}} = E^\circ_{\mathrm{Ag^+/Ag}} - 0 = E^\circ_{\mathrm{Ag^+/Ag}}$$

It is important to note that the potential is *not* doubled for the cathode reaction.

The SHE is rather dangerous and rarely used in the laboratory. Its main significance is that it established the zero for standard reduction potentials. Once determined, standard reduction potentials can be used to determine the standard cell potential, E°_{cell}, for any cell. For example, for the following cell:

$$\mathrm{Cu}(s)\,|\,\mathrm{Cu^{2+}}(aq,\ 1\ M)\,\|\,\mathrm{Ag^+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s)$$

$$\begin{array}{l}\text{anode (oxidation): } \mathrm{Cu}(s) \longrightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{e^-} \\ \text{cathode (reduction): } 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}(s) \\ \hline \text{overall: } \mathrm{Cu}(s) + 2\,\mathrm{Ag^+}(aq) \longrightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{Ag}(s)\end{array}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{Cu^{2+}/Cu}} = 0.80\ \mathrm{V} - 0.34\ \mathrm{V} = 0.46\ \mathrm{V}$$

Again, note that when calculating E°_{cell}, standard reduction potentials always remain the same even when a half-reaction is multiplied by a factor. Standard reduction potentials for selected reduction reactions are shown in Table 9.3.1. A more complete list is provided in Tables P1 or P2.

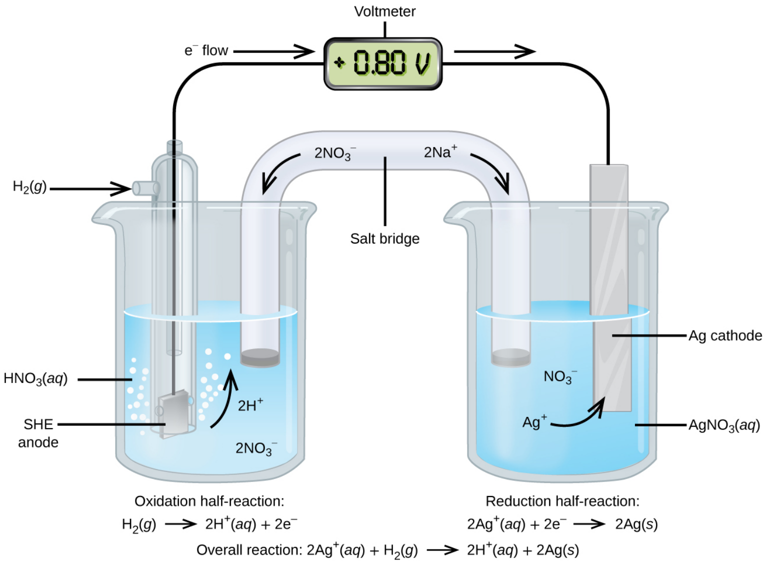

Figure 9.3.3: A galvanic cell can be used to determine the standard reduction potential of Ag^+. The SHE on the left is the anode and assigned a standard reduction potential of zero.

Table 9.3.1: Selected Standard Reduction Potentials at 25 °C

Half-Reaction	**E° (V)**
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.866
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$	+1.69
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.507
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.498
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.35827
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+1.229
$Pt^{2+}(aq) + 2e^- \longrightarrow Pt(s)$	+1.20
$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$	+1.0873
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.7996
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.7973
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.558
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.5355
$NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq)$	+0.26808
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22233
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.151
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.1262
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.1375

Half-Reaction	E° (V)
$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$	−0.257
$Co^{2+}(aq) + 2\,e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2\,e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.3505
$Cd^{2+}(aq) + 2\,e^- \longrightarrow Cd(s)$	−0.4030
$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$	−0.447
$Cr^{3+}(aq) + 3\,e^- \longrightarrow Cr(s)$	−0.744
$Mn^{2+}(aq) + 2\,e^- \longrightarrow Mn(s)$	−1.185
$Zn(OH)_2(s) + 2\,e^- \longrightarrow Zn(s) + 2\,OH^-(aq)$	−1.245
$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	−0.7618
$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$	−1.662
$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$	−2.372
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2\,e^- \longrightarrow Ca(s)$	−2.868
$Ba^{2+}(aq) + 2\,e^- \longrightarrow Ba(s)$	−2.912
$K^+(aq) + e^- \longrightarrow K(s)$	−2.931
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.04

Tables like this make it possible to determine the standard cell potential for many oxidation-reduction reactions.

✓ Example 9.3.1: Cell Potentials from Standard Reduction Potentials

What is the standard cell potential for a galvanic cell that consists of Au^{3+}/Au and Ni^{2+}/Ni half-cells? Identify the oxidizing and reducing agents.

Solution

Using Table 9.3.1, the reactions involved in the galvanic cell, both written as reductions, are

$$Au^{3+}(aq) + 3\,e^- \longrightarrow Au(s) \qquad E^\circ_{Au^{3+}/Au} = +1.498\text{ V}$$

$$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s) \qquad E^\circ_{Ni^{2+}/Ni} = -0.257\text{ V}$$

Galvanic cells have positive cell potentials, and all the reduction reactions are reversible. The reaction at the anode will be the half-reaction with the smaller or more negative standard reduction potential. Reversing the reaction at the anode (to show the oxidation) but *not* its standard reduction potential gives:

$$\text{Anode (oxidation): } Ni(s) \longrightarrow Ni^{2+}(aq) + 2\,e^- \qquad E^\circ_{\text{anode}} = E^\circ_{Ni^{2+}/Ni} = -0.257\text{ V}$$

$$\text{Cathode (reduction): } Au^{3+}(aq) + 3\,e^- \longrightarrow Au(s) \qquad E^\circ_{\text{cathode}} = E^\circ_{Au^{3+}/Au} = +1.498\text{ V}$$

The least common factor is six, so the overall reaction is

$$3\,Ni(s) + 2\,Au^{3+}(aq) \longrightarrow 3\,Ni^{2+}(aq) + 2\,Au(s)$$

The reduction potentials are *not* scaled by the stoichiometric coefficients when calculating the cell potential, and the unmodified standard reduction potentials must be used.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 1.498\text{ V} - (-0.257\text{ V}) = 1.755\text{ V}$$

From the half-reactions, Ni is oxidized, so it is the reducing agent, and Au^{3+} is reduced, so it is the oxidizing agent.

Exercise 9.3.1

A galvanic cell consists of a Mg electrode in 1 *M* $Mg(NO_3)_2$ solution and a Ag electrode in 1 *M* $AgNO_3$ solution. Calculate the standard cell potential at 25 °C.

Answer

$$\mathrm{Mg}(s) + 2\,\mathrm{Ag}^+(aq) \longrightarrow \mathrm{Mg}^{2+}(aq) + 2\,\mathrm{Ag}(s) \qquad E^\circ_{\mathrm{cell}} = 0.7996\ \mathrm{V} - (-2.372\ \mathrm{V}) = 3.172\ \mathrm{V}$$

Summary

Assigning the potential of the standard hydrogen electrode (SHE) as zero volts allows the determination of standard reduction potentials, $E°$, for half-reactions in electrochemical cells. As the name implies, standard reduction potentials use standard states (1 bar or 1 atm for gases; 1 *M* for solutes, often at 298.15 K) and are written as reductions (where electrons appear on the left side of the equation). The reduction reactions are reversible, so standard cell potentials can be calculated by subtracting the standard reduction potential for the reaction at the anode from the standard reduction for the reaction at the cathode. When calculating the standard cell potential, the standard reduction potentials are *not* scaled by the stoichiometric coefficients in the balanced overall equation.

9.3.1: Key Equations

- $E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{cathode}} - E^\circ_{\mathrm{anode}}$

Glossary

standard cell potential (E°_{cell})

the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 *M* for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

standard hydrogen electrode (SHE)

the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

standard reduction potential ($E°$)

the value of the reduction under standard conditions (1 bar or 1 atm for gases; 1 *M* for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials

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9.4: The Nernst Equation

Learning Objectives

- Relate cell potentials to free 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

We will now extend electrochemistry by determining the relationship between E°_{cell} and the thermodynamics quantities such as $\Delta G°$ (Gibbs free energy) and K (the equilibrium constant). In galvanic cells, chemical energy is converted into electrical energy, which can do work. The electrical work is the product of the charge transferred multiplied by the potential difference (voltage):

$$\text{electrical work} = \text{volts} \times (\text{charge in coulombs}) = \text{J}$$

The charge on 1 mole of electrons is given by Faraday's constant (F)

$$\begin{aligned} F &= \frac{6.022 \times 10^{23}\ e^-}{mol} \times \frac{1.602 \times 10^{-19}\ C}{e^-} \\ &= 9.648 \times 10^4\ \frac{C}{mol} \\ &= 9.648 \times 10^4\ \frac{J}{V \cdot mol} \end{aligned}$$

Therefore

$$\text{total charge} = (\text{number of moles of e}^-) \times F = nF$$

In this equation, n is the number of moles of electrons for the *balanced* oxidation-reduction reaction. The measured cell potential is the maximum potential the cell can produce and is related to the electrical work (w_{ele}) by

$$E_{\text{cell}} = \frac{-w_{\text{ele}}}{nF} \qquad \text{or} \qquad w_{\text{ele}} = -nFE_{\text{cell}}$$

The negative sign for the work indicates that the electrical work is done by the system (the galvanic cell) on the surroundings. In an earlier chapter, the free energy was defined as the energy that was available to do work. In particular, the change in free energy was defined in terms of the maximum work (w_{max}), which, for electrochemical systems, is w_{ele}.

$$\begin{aligned} \Delta G &= w_{\text{max}} = w_{\text{ele}} \\ &= -nFE_{\text{cell}} \end{aligned}$$

We can verify the signs are correct when we realize that n and F are positive constants and that galvanic cells, which have positive cell potentials, involve spontaneous reactions. Thus, spontaneous reactions, which have $\Delta G < 0$, must have $E_{cell} > 0$. If all the reactants and products are in their standard states, this becomes

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

This provides a way to relate standard cell potentials to equilibrium constants, since

$$\Delta G^\circ = -RT \ln K$$

$$-nFE^\circ_{\text{cell}} = -RT \ln K$$

or

$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K$$

Most of the time, the electrochemical reactions are run at standard temperature (298.15 K). Collecting terms at this temperature yields

$$\begin{aligned} E^\circ_\text{cell} &= \frac{RT}{nF}\ln K \\ &= \frac{\left(8.314\ \frac{\text{J}}{\text{K}\cdot\text{mol}}\right)(298.15\ K)}{n \times 96,485\ \text{C}/\text{V}\cdot\text{mol}}\ln K \\ &= \frac{0.0257\ \text{V}}{n}\ln K \end{aligned}$$

where n is the number of moles of electrons. The logarithm in equations involving cell potentials is often expressed using base 10 logarithms (i.e., $\log_{10}$ or just log), which changes the constant by a factor of 2.303:

$$E^\circ_\text{cell} = \frac{0.0592\ \text{V}}{n}\log K$$

Thus, if $\Delta G°$, K, or E°_cell is known or can be calculated, the other two quantities can be readily determined. The relationships are shown graphically in Figure 9.4.1.

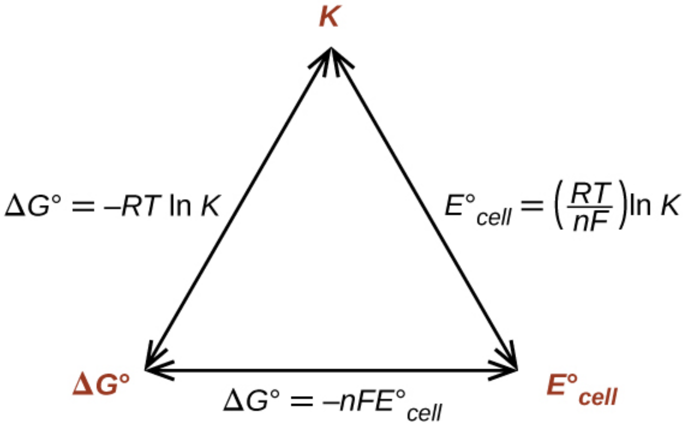

Figure 9.4.1: The relationships between ΔG°, K, and E°_cell. *Given any one of the three quantities, the other two can be calculated, so any of the quantities could be used to determine whether a process was spontaneous.*

A diagram is shown that involves three double headed arrows positioned in the shape of an equilateral triangle. The vertices are labeled in red. The top vertex is labeled “K.“ The vertex at the lower left is labeled “delta G superscript degree symbol.” The vertex at the lower right is labeled “E superscript degree symbol subscript cell.” The right side of the triangle is labeled “E superscript degree symbol subscript cell equals (R T divided by n F) l n K.” The lower side of the triangle is labeled “delta G superscript degree symbol equals negative n F E superscript degree symbol subscript cell.” The left side of the triangle is labeled “delta G superscript degree symbol equals negative R T l n K.”

Given any one of the quantities, the other two can be calculated.

✓ Example 9.4.1: Equilibrium Constants, Potentials, & Free Energy Changes

What is the standard Gibbs free energy change and equilibrium constant for the following reaction at 25 °C?

$$2\ \text{Ag}^+(aq) + \text{Fe}(s) \rightleftharpoons 2\ \text{Ag}(s) + \text{Fe}^{2+}(aq)$$

Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in Table P1.

$$\begin{aligned} &\text{anode (oxidation): Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2\ \text{e}^- \qquad E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.447\ \text{V} \\ &\text{cathode (reduction): } 2 \times (\text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)) \qquad E^\circ_{\text{Ag}^+/\text{Ag}} = 0.7996\ \text{V} \\ &E^\circ_\text{cell} = E^\circ_\text{cathode} - E^\circ_\text{anode} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Fe}^{2+}/\text{Fe}} = +1.247\ \text{V} \end{aligned}$$

Remember that the cell potential for the cathode is not multiplied by two when determining the standard cell potential. With $n = 2$, the equilibrium constant is then

$$E^\circ_{\text{cell}} = \frac{0.0592 \text{ V}}{n} \log K$$

$$K = 10^{n \times E^\circ_{\text{cell}}/0.0592 \text{ V}}$$

$$= 10^{2 \times 1.247 \text{ V}/0.0592 \text{ V}}$$

$$= 10^{42.128}$$

$$= 1.3 \times 10^{42}$$

The standard free energy is then

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta G^\circ = -2 \times 96,485 \frac{\text{J}}{\text{V}\cdot\text{mol}} \times 1.247 \text{ V} = -240.6 \frac{\text{kJ}}{\text{mol}}$$

Check your answer: A positive standard cell potential means a spontaneous reaction, so the standard free energy change should be negative, and an equilibrium constant should be >1.

? Exercise 9.4.1

What is the standard Gibbs free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?

$$\text{Sn}(s) + 2\,\text{Cu}^{2+}(aq) \rightleftharpoons \text{Sn}^{2+}(aq) + 2\,\text{Cu}^{+}(aq)$$

Answer

Spontaneous; $n = 2$; $E^\circ_{\text{cell}} = +0.291 \text{ V}$; $\Delta G^\circ = -56.2 \frac{\text{kJ}}{\text{mol}}$; $K = 6.8 \times 10^9$.

Now that the connection has been made between the free energy and cell potentials, nonstandard concentrations follow. Recall that

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where Q is the reaction quotient (see the chapter on equilibrium fundamentals). Converting to cell potentials:

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + RT \ln Q \tag{9.4.1}$$

or

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q \tag{9.4.2}$$

Equation 9.4.2 is the generalized Nernst equation that is applicable at any temperature. However, is can be simplified for reactions occuring at 25 °C (298.15 K) by rewriting it as

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0257 \text{ V}}{n} \ln Q \tag{9.4.3}$$

or

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592 \text{ V}}{n} \log_{10} Q \tag{9.4.4}$$

If the temperature is not 298.15 K, it is necessary to recalculate the potential with Equation 9.4.2. With the Nernst equation, it is possible to calculate the cell potential at nonstandard conditions. This adjustment is necessary because potentials determined under different conditions will have different values.

✓ Example 9.4.2: Cell Potentials at Nonstandard Conditions

Consider the following reaction at room temperature:

$$\mathrm{Co}(s)+\mathrm{Fe}^{2+}(aq,\ 1.94\ M)\longrightarrow \mathrm{Co}^{2+}(aq,\ 0.15\ M)+\mathrm{Fe}(s)$$

Is the process spontaneous?

Solution

There are two ways to solve the problem. If the thermodynamic information in Table T1 were available, you could calculate the free energy change. If the free energy change is negative, the process is spontaneous. The other approach, which we will use, requires information like that given in Table P1. Using those data, the cell potential can be determined. If the cell potential is positive, the process is spontaneous. Collecting information from Table P1 and the problem,

$$\begin{aligned}
&\text{Anode (oxidation): }\mathrm{Co}(s)\longrightarrow \mathrm{Co}^{2+}(aq)+2\,\mathrm{e}^- && E^\circ_{\mathrm{Co}^{2+}/\mathrm{Co}}=-0.28\ \mathrm{V}\\
&\text{Cathode (reduction): }\mathrm{Fe}^{2+}(aq)+2\,\mathrm{e}^-\longrightarrow \mathrm{Fe}(s) && E^\circ_{\mathrm{Fe}^{2+}/\mathrm{Fe}}=-0.447\ \mathrm{V}\\
&E^\circ_{\text{cell}}=E^\circ_{\text{cathode}}-E^\circ_{\text{anode}}=-0.447\ \mathrm{V}-(-0.28\ \mathrm{V})=-0.17\ \mathrm{V}
\end{aligned}$$

The process is not spontaneous under standard conditions. Using the Nernst equation and the concentrations stated in the problem and $n=2$,

$$Q=\frac{[\mathrm{Co}^{2+}]}{[\mathrm{Fe}^{2+}]}=\frac{0.15\ M}{1.94\ M}=0.077$$

Now we can insert these into the Nernst Equation at room temperature (Equation 9.4.4)

$$\begin{aligned}
E_{\text{cell}}&=E^\circ_{\text{cell}}-\frac{0.0592\ \mathrm{V}}{n}\log Q\\
&=-0.17\ \mathrm{V}-\frac{0.0592\ \mathrm{V}}{2}\log 0.077\\
&=-0.17\ \mathrm{V}+0.033\ \mathrm{V}=-0.14\ \mathrm{V}
\end{aligned}$$

The process is (still) nonspontaneous.

? Exercise 9.4.2

What is the cell potential for the following reaction at room temperature?

$$\mathrm{Al}(s)\,|\,\mathrm{Al}^{3+}(aq,\ 0.15\ M)\,\|\,\mathrm{Cu}^{2+}(aq,\ 0.025\ M)\,|\,\mathrm{Cu}(s)$$

What are the values of n and Q for the overall reaction? Is the reaction spontaneous under these conditions?

Answer

n = 6; Q = 1440; E_{cell} = +1.97 V, spontaneous.

Finally, we will take a brief look at a special type of cell called a concentration cell. In a concentration cell, the electrodes are the same material and the half-cells differ only in concentration. Since one or both compartments is not standard, the cell potentials will be unequal; therefore, there will be a potential difference, which can be determined with the aid of the Nernst equation.

✓ Example 9.4.3: Concentration Cells

What is the cell potential of the concentration cell described by

$$\mathrm{Zn}(s)\,|\,\mathrm{Zn}^{2+}(aq,\ 0.10\ M)\,\|\,\mathrm{Zn}^{2+}(aq,\ 0.50\ M)\,|\,\mathrm{Zn}(s)$$

Solution

From the information given:

$$\begin{array}{ll}\text{Anode: } \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq,\ 0.10\ M) + 2\,\mathrm{e}^{-} & E^{\circ}_{\text{anode}} = -0.7618\ \mathrm{V} \\ \text{Cathode: } \mathrm{Zn}^{2+}(aq,\ 0.50\ M) + 2\,\mathrm{e}^{-} \longrightarrow \mathrm{Zn}(s) & E^{\circ}_{\text{cathode}} = -0.7618\ \mathrm{V} \\ \hline \text{Overall: } \mathrm{Zn}^{2+}(aq,\ 0.50\ M) \longrightarrow \mathrm{Zn}^{2+}(aq,\ 0.10\ M) & E^{\circ}_{\text{cell}} = 0.000\ \mathrm{V}\end{array}$$

The standard cell potential is zero because the anode and cathode involve the same reaction; only the concentration of Zn^{2+} changes. Substituting into the Nernst equation,

$$E_{\text{cell}} = 0.000\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{2} \log \frac{0.10}{0.50} = +0.021\ \mathrm{V}$$

and the process is spontaneous at these conditions.

Check your answer: In a concentration cell, the standard cell potential will always be zero. To get a positive cell potential (spontaneous process) the reaction quotient Q must be <1. $Q < 1$ in this case, so the process is spontaneous.

? Exercise 9.4.3

What value of Q for the previous concentration cell would result in a voltage of 0.10 V? If the concentration of zinc ion at the cathode was 0.50 *M*, what was the concentration at the anode?

Answer

Q = 0.00042; $[Zn^{2+}]_{cat}$ = 2.1 \times 10^{-4} *M*.

Summary

Electrical work (w_{ele}) is the negative of the product of the total charge (Q) and the cell potential (E_{cell}). The total charge can be calculated as the number of moles of electrons (n) times the Faraday constant (F = 96,485 C/mol e^-). Electrical work is the maximum work that the system can produce and so is equal to the change in free energy. Thus, anything that can be done with or to a free energy change can also be done to or with a cell potential. The Nernst equation relates the cell potential at nonstandard conditions to the logarithm of the reaction quotient. Concentration cells exploit this relationship and produce a positive cell potential using half-cells that differ only in the concentration of their solutes.

9.4.1: Key Equations

- $E^{\circ}_{\text{cell}} = \frac{RT}{nF} \ln K$
- $E^{\circ}_{\text{cell}} = \frac{0.0257\ \mathrm{V}}{n} \ln K = \frac{0.0592\ \mathrm{V}}{n} \log K \qquad (\text{at } 298.15\ K)$
- $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q \qquad (\text{Nernst equation})$
- $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0257\ V}{n} \ln Q = E^{\circ}_{\text{cell}} - \frac{0.0592\ \mathrm{V}}{n} \log Q \qquad (\text{at } 298.15\ K)$
- $\Delta G = -nFE_{cell}$
- $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$
- $w_{\text{ele}} = w_{\text{max}} = -nFE_{\text{cell}}$

Glossary

concentration cell

galvanic cell in which the two half-cells are the same except for the concentration of the solutes; spontaneous when the overall reaction is the dilution of the solute

electrical work (w_{ele})

negative of total charge times the cell potential; equal to w_{max} for the system, and so equals the free energy change (ΔG)

Faraday's constant (F)

charge on 1 mol of electrons; F = 96,485 C/mol e^-

Nernst equation

equation that relates the logarithm of the reaction quotient (Q) to nonstandard cell potentials; can be used to relate equilibrium constants to standard cell potentials

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9.5: Batteries and Fuel Cells

Learning Objectives

- Classify batteries as primary or secondary
- List some of the characteristics and limitations of batteries
- Provide a general description of a fuel cell

A battery is an electrochemical cell or series of cells that produces an electric current. In principle, any galvanic cell could be used as a battery. An ideal battery would never run down, produce an unchanging voltage, and be capable of withstanding environmental extremes of heat and humidity. Real batteries strike a balance between ideal characteristics and practical limitations. For example, the mass of a car battery is about 18 kg or about 1% of the mass of an average car or light-duty truck. This type of battery would supply nearly unlimited energy if used in a smartphone, but would be rejected for this application because of its mass. Thus, no single battery is "best" and batteries are selected for a particular application, keeping things like the mass of the battery, its cost, reliability, and current capacity in mind. There are two basic types of batteries: primary and secondary. A few batteries of each type are described next.

> *Visit this site to learn more about batteries.*

9.5.0.0.1: Primary Batteries

Primary batteries are single-use batteries because they cannot be recharged. A common primary battery is the dry cell (Figure 9.5.1). The dry cell is a zinc-carbon battery. The zinc can serves as both a container and the negative electrode. The positive electrode is a rod made of carbon that is surrounded by a paste of manganese(IV) oxide, zinc chloride, ammonium chloride, carbon powder, and a small amount of water. The reaction at the anode can be represented as the ordinary oxidation of zinc:

$$\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + 2\,\mathrm{e}^- \qquad E^\circ_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = -0.7618\ \mathrm{V}$$

The reaction at the cathode is more complicated, in part because more than one reaction occurs. The series of reactions that occurs at the cathode is approximately

$$2\,\mathrm{MnO}_2(s) + 2\,\mathrm{NH}_4\mathrm{Cl}(aq) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Mn}_2\mathrm{O}_3(s) + 2\,\mathrm{NH}_3(aq) + \mathrm{H}_2\mathrm{O}(l) + 2\,\mathrm{Cl}^-$$

The overall reaction for the zinc–carbon battery can be represented as

$$2\,\mathrm{MnO}_2(s) + 2\,\mathrm{NH}_4\mathrm{Cl}(aq) + \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Mn}_2\mathrm{O}_3(s) + 2\,\mathrm{NH}_3(aq) + \mathrm{H}_2\mathrm{O}(l) + 2\,\mathrm{Cl}^-$$

with an overall cell potential which is initially about 1.5 V, but decreases as the battery is used. It is important to remember that the voltage delivered by a battery is the same regardless of the size of a battery. For this reason, D, C, A, AA, and AAA batteries all have the same voltage rating. However, larger batteries can deliver more moles of electrons. As the zinc container oxidizes, its contents eventually leak out, so this type of battery should not be left in any electrical device for extended periods.

Figure 9.5.1: The diagram shows a cross section of a flashlight battery, a zinc-carbon dry cell.

A diagram of a cross section of a dry cell battery is shown. The overall shape of the cell is cylindrical. The lateral surface of the cylinder, indicated as a thin red line, is labeled "zinc can (electrode)." Just beneath this is a slightly thicker dark grey surface that covers the lateral surface, top, and bottom of the battery, which is labeled "Porous separator." Inside is a purple region with many evenly spaced small darker purple dots, labeled "Paste of M n O subscript 2, N H subscript 4 C l, Z n C l subscript 2, water (cathode)." A dark grey rod, labeled "Carbon rod (electrode)," extends from the top of the battery, leaving a gap of less than one-fifth the height of the battery below the rod to the bottom of the cylinder. A thin grey line segment at the very bottom of the cylinder is labeled "Metal bottom cover (negative)." The very top of the cylinder has a thin grey surface that curves upward at the center over the top of the carbon electrode at the center of the cylinder. This upper surface is labeled "Metal top cover (positive)." A thin dark grey line just below this surface is labeled "Insulator." Below this, above the purple region, and outside of the carbon electrode at the center is an orange region that is labeled "Seal."

Alkaline batteries (Figure 9.5.2) were developed in the 1950s partly to address some of the performance issues with zinc–carbon dry cells. They are manufactured to be exact replacements for zinc-carbon dry cells. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are

$$\begin{array}{ll} \text{anode: } \mathrm{Zn}(s) + 2\,\mathrm{OH^-}(aq) \longrightarrow \mathrm{ZnO}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{e^-} & E^\circ_{\text{anode}} = -1.28\text{ V} \\ \underline{\text{cathode: } 2\,\mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Mn_2O_3}(s) + 2\,\mathrm{OH^-}(aq)} & \underline{E^\circ_{\text{cathode}} = +0.15\text{ V}} \\ \text{overall: } \mathrm{Zn}(s) + 2\,\mathrm{MnO_2}(s) \longrightarrow \mathrm{ZnO}(s) + \mathrm{Mn_2O_3}(s) & E^\circ_{\text{cell}} = +1.43\text{ V} \end{array}$$

An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so these should also be removed from devices for long-term storage. While some alkaline batteries are rechargeable, most are not. Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.

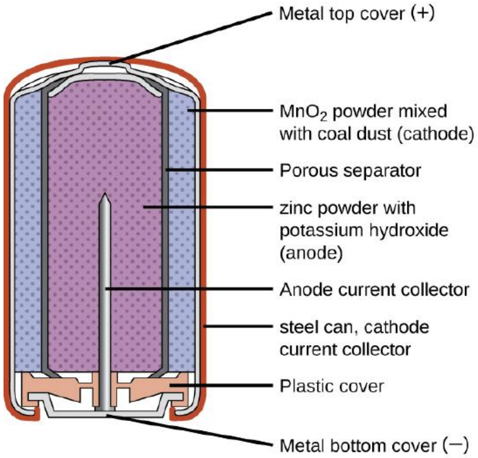

Figure 9.5.2: Alkaline batteries were designed as direct replacements for zinc-carbon (dry cell) batteries.

9.5.0.0.1: Secondary Batteries

Secondary batteries are rechargeable. These are the types of batteries found in devices such as smartphones, electronic tablets, and automobiles.

Nickel-cadmium, or NiCd, batteries (Figure 9.5.3) consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a “jelly-roll” design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. The reactions are

$$\begin{array}{l} \text{anode: } \mathrm{Cd}(s) + 2\,\mathrm{OH^-}(aq) \longrightarrow \mathrm{Cd(OH)_2}(s) + 2\,\mathrm{e^-} \\ \underline{\text{cathode: } \mathrm{NiO_2}(s) + 2\,\mathrm{H_2O}(l) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Ni(OH)_2}(s) + 2\,\mathrm{OH^-}(aq)} \\ \text{overall: } \mathrm{Cd}(s) + \mathrm{NiO_2}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{Cd(OH)_2}(s) + \mathrm{Ni(OH)_2}(s) \end{array}$$

The voltage is about 1.2 V to 1.25 V as the battery discharges. When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be opened or put into the regular trash.

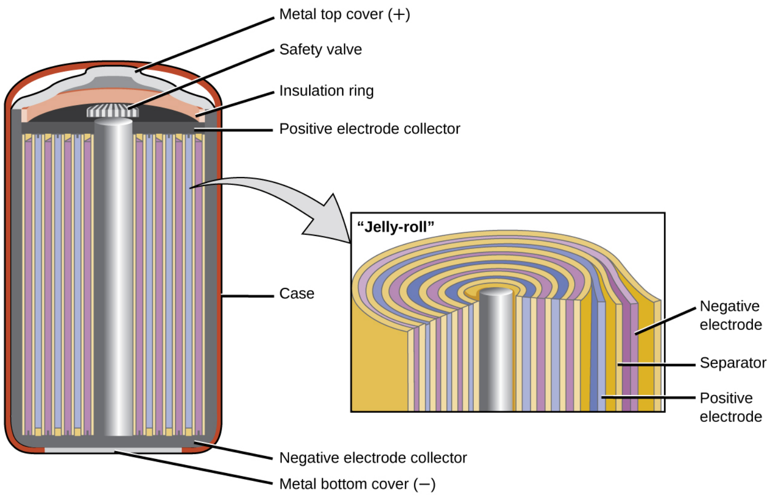

Figure 9.5.3: NiCd batteries use a "jelly-roll" design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.

Lithium ion batteries (Figure 9.5.4) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

$$\begin{array}{l} \text{anode: } \mathrm{LiCoO_2} \rightleftharpoons \mathrm{Li_{1-\mathit{x}}CoO_2} + x\mathrm{Li^+} + x\mathrm{e^-} \\ \text{cathode: } x\mathrm{Li^+} + x\mathrm{e^-} + x\mathrm{C_6} \rightleftharpoons x\mathrm{LiC_6} \\ \hline \text{overall: } \mathrm{LiCoO_2} + x\mathrm{C_6} \rightleftharpoons \mathrm{Li_{1-\mathit{x}}CoO_2} + x\mathrm{LiC_6} \end{array}$$

With the coefficients representing moles, *x* is no more than about 0.5 moles. The battery voltage is about 3.7 V. Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

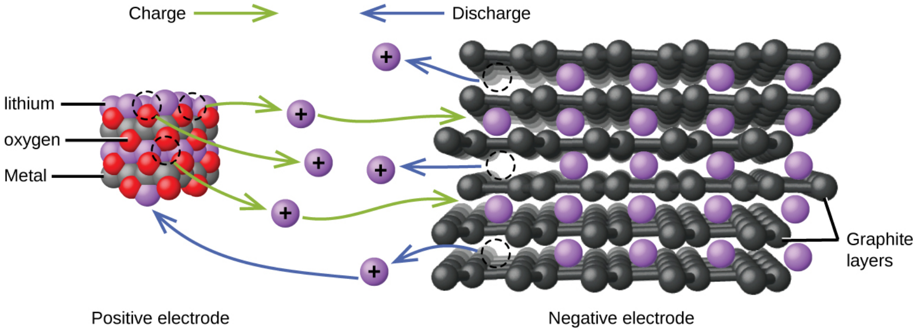

Figure 9.5.4: In a lithium ion battery, charge flows between the electrodes as the lithium ions move between the anode and cathode.

The lead acid battery (Figure 9.5.5) is the type of secondary battery used in your automobile. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are

$$\begin{array}{l} \text{anode: } \mathrm{Pb}(s) + \mathrm{HSO_4^-}(aq) \longrightarrow \mathrm{PbSO_4}(s) + \mathrm{H^+}(aq) + 2\,\mathrm{e^-} \\ \text{cathode: } \mathrm{PbO_2}(s) + \mathrm{HSO_4^-}(aq) + 3\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{PbSO_4}(s) + 2\,\mathrm{H_2O}(l) \\ \hline \text{overall: } \mathrm{Pb}(s) + \mathrm{PbO_2}(s) + 2\,\mathrm{H_2SO_4}(aq) \longrightarrow 2\,\mathrm{PbSO_4}(s) + 2\,\mathrm{H_2O}(l) \end{array}$$

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

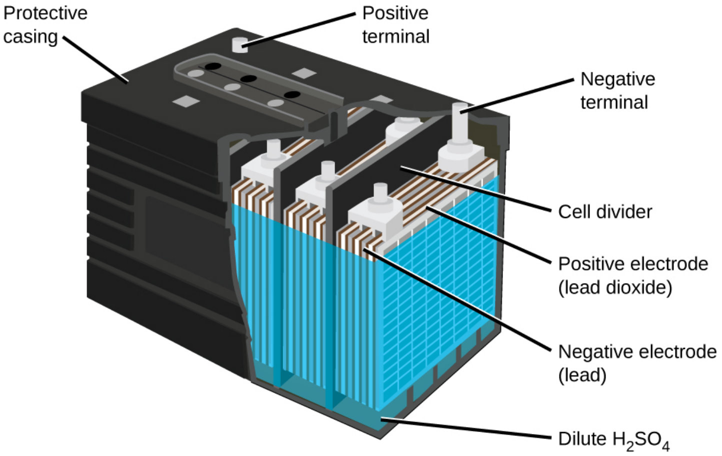

Figure 9.5.5: The lead acid battery in your automobile consists of six cells connected in series to give 12 V. Their low cost and high current output makes these excellent candidates for providing power for automobile starter motors.

9.5.1: Fuel Cells

A fuel cell is a device that converts chemical energy into electrical energy. Fuel cells are similar to batteries but require a continuous source of fuel, often hydrogen. They will continue to produce electricity as long as fuel is available. Hydrogen fuel cells have been used to supply power for satellites, space capsules, automobiles, boats, and submarines (Figure 9.5.6).

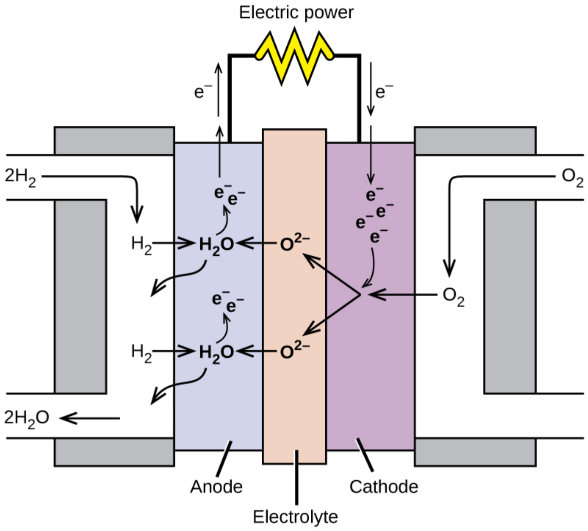

Figure 9.5.6: In this hydrogen fuel-cell schematic, oxygen from the air reacts with hydrogen, producing water and electricity.

In a hydrogen fuel cell, the reactions are

$$\begin{array}{l} \text{anode: } 2\,H_2 + 2\,O^{2-} \longrightarrow 2\,H_2O + 4\,e^- \\ \underline{\text{cathode: } O_2 + 4\,e^- \longrightarrow 2\,O^{2-}\qquad\qquad} \\ \text{overall: } 2\,H_2 + O_2 \longrightarrow 2\,H_2O \end{array}$$

The voltage is about 0.9 V. The efficiency of fuel cells is typically about 40% to 60%, which is higher than the typical internal combustion engine (25% to 35%) and, in the case of the hydrogen fuel cell, produces only water as exhaust. Currently, fuel cells are rather expensive and contain features that cause them to fail after a relatively short time.

Summary

Batteries are galvanic cells, or a series of cells, that produce an electric current. When cells are combined into batteries, the potential of the battery is an integer multiple of the potential of a single cell. There are two basic types of batteries: primary and secondary. Primary batteries are “single use” and cannot be recharged. Dry cells and (most) alkaline batteries are examples of primary batteries. The second type is rechargeable and is called a secondary battery. Examples of secondary batteries include nickel-cadmium (NiCd), lead acid, and lithium ion batteries. Fuel cells are similar to batteries in that they generate an electrical current, but require continuous addition of fuel and oxidizer. The hydrogen fuel cell uses hydrogen and oxygen from the air to produce water, and is generally more efficient than internal combustion engines.

Summary

alkaline battery

primary battery that uses an alkaline (often potassium hydroxide) electrolyte; designed to be an exact replacement for the dry cell, but with more energy storage and less electrolyte leakage than typical dry cell

battery

galvanic cell or series of cells that produces a current; in theory, any galvanic cell

dry cell

primary battery, also called a zinc-carbon battery; can be used in any orientation because it uses a paste as the electrolyte; tends to leak electrolyte when stored

fuel cell

devices that produce an electrical current as long as fuel and oxidizer are continuously added; more efficient than internal combustion engines

lead acid battery

secondary battery that consists of multiple cells; the lead acid battery found in automobiles has six cells and a voltage of 12 V

lithium ion battery

very popular secondary battery; uses lithium ions to conduct current and is light, rechargeable, and produces a nearly constant potential as it discharges

nickel-cadmium battery

(NiCd battery) secondary battery that uses cadmium, which is a toxic heavy metal; heavier than lithium ion batteries, but with similar performance characteristics

primary battery

single-use nonrechargeable battery

secondary battery

battery that can be recharged

9.6: Corrosion

Learning Objectives

- Define corrosion
- List some of the methods used to prevent or slow corrosion

Corrosion is usually defined as the degradation of metals due to an electrochemical process. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper are all examples of corrosion. The total cost of corrosion in the United States is significant, with estimates in excess of half a trillion dollars a year.

Changing Colors

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green color. When this statue was first delivered from France, its appearance was not green. It was brown, the color of its copper "skin." So how did the Statue of Liberty change colors? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occur in several steps. Copper metal is oxidized to copper(I) oxide ($\mathrm{Cu_2O}$), which is red, and then to copper(II) oxide, which is black.

$$2\,\mathrm{Cu(s)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \underset{\text{red}}{\mathrm{Cu_2O(s)}}$$

$$\mathrm{Cu_2O(s)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \underset{\text{black}}{2\,\mathrm{CuO(s)}}$$

Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, sulfur trioxide, carbon dioxide, and water all reacted with the CuO.

$$2\,\mathrm{CuO(s)} + \mathrm{CO_2(g)} + \mathrm{H_2O(l)} \rightarrow \underset{\text{green}}{\mathrm{Cu_2CO_3(OH)_2(s)}}$$

$$3\,\mathrm{CuO(s)} + 2\,\mathrm{CO_2(g)} + \mathrm{H_2O(l)} \rightarrow \underset{\text{blue}}{\mathrm{Cu_2(CO_3)_2(OH)_2(s)}}$$

$$4\,\mathrm{CuO(s)} + \mathrm{SO_3(g)} + 3\,\mathrm{H_2O(l)} \rightarrow \underset{\text{green}}{\mathrm{Cu_4SO_4(OH)_6(s)}}$$

These three compounds are responsible for the characteristic blue-green patina seen today. Fortunately, formation of the patina created a protective layer on the surface, preventing further corrosion of the copper skin. The formation of the protective layer is a form of passivation, which is discussed further in a later chapter.

This figure contains two photos of the Statue of Liberty. Photo a appears to be an antique photo which shows the original brown color of the copper covered statue. Photo b shows the blue-green appearance of the statue today. In both photos, the statue is shown atop a building, with a body of water in the background."

Figure 9.6.1: (a) The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today.

Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. The main steps in the rusting of iron appear to involve the following. Once exposed to the atmosphere, iron rapidly oxidizes.

$$\text{anode: } \mathrm{Fe}_{(s)} \rightarrow \mathrm{Fe}^{2+}_{(aq)} + 2\,\mathrm{e}^- \quad E^\circ_{\mathrm{Fe^{2+}/Fe}} = -0.44\ \mathrm{V}$$

The electrons reduce oxygen in the air in acidic solutions.

$$\text{cathode: } \mathrm{O}_{2(g)} + 4\,\mathrm{H}^+_{(aq)} + 4\,\mathrm{e}^- \rightarrow 2\,\mathrm{H_2O}_{(l)} \quad E^\circ_{\mathrm{O_2/O_2}} = +1.23\ \mathrm{V}$$

$$\text{overall: } 2\,\mathrm{Fe}_{(s)} + \mathrm{O}_{2(g)} + 4\,\mathrm{H}^+_{(aq)} \rightarrow 2\,\mathrm{Fe}^{2+}_{(aq)} + 2\,\mathrm{H_2O}_{(l)} \quad E^\circ_{\text{cell}} = +1.67\ \mathrm{V}$$

What we call rust is hydrated iron(III) oxide, which forms when iron(II) ions react further with oxygen.

$$4\,\mathrm{Fe}^{2+}_{(aq)} + \mathrm{O}_{2(g)} + (4+2x)\mathrm{H_2O}_{(l)} \rightarrow 2\,\mathrm{Fe_2O_3}\cdot x\mathrm{H_2O}_{(s)} + 8\,\mathrm{H}^+_{(aq)}$$

The number of water molecules is variable, so it is represented by *x*. Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.

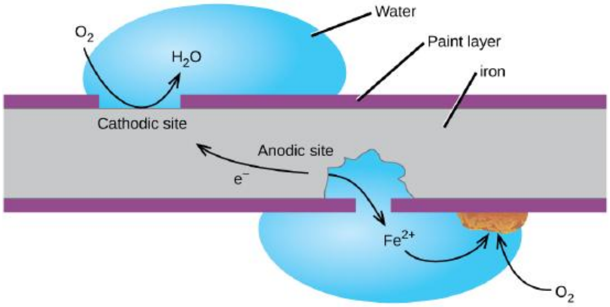

Figure 9.6.2: Once the paint is scratched on a painted iron surface, corrosion occurs and rust begins to form. The speed of the spontaneous reaction is increased in the presence of electrolytes, such as the sodium chloride used on roads to melt ice and snow or in salt water.

A grey rectangle, labeled “iron,” is shown with thin purple layers, labeled “Paint layer,” at its upper and lower surfaces. A gap in the upper purple layer at the upper left of the diagram is labeled “Cathodic site.” A blue droplet labeled “water” is positioned on top of the gap. A curved arrow extends from a space above the droplet to the surface of the grey region and into the water droplet. The base of the arrow is labeled “O subscript 2” and the tip of the arrow is labeled “H subscript 2 O.” A gap to the right and on the bottom side of the grey region shows that some of the grey region is gone from the region beneath the purple layer. A water droplet covers this gap and extends into the open space in the grey rectangle. The label “F e superscript 2 positive” is at the center of the droplet. A curved arrow points from the edge of the grey area below to the label. A second curved arrow extends from the F e superscript 2 positive arrow to a rust brown chunk on the lower surface of the purple layer at the edge of the water droplet. A curved arrow extends from O subscript 2 outside the droplet into the droplet to the rust brown chunk. The grey region at the lower right portion of the diagram is labeled “Anodic site.” An arrow extends from the anodic site toward the cathodic site, which is labeled “e superscript negative.”

One way to keep iron from corroding is to keep it painted. The layer of paint prevents the water and oxygen necessary for rust formation from coming into contact with the iron. As long as the paint remains intact, the iron is protected from corrosion.

Other strategies include alloying the iron with other metals. For example, stainless steel is mostly iron with a bit of chromium. The chromium tends to collect near the surface, where it forms an oxide layer that protects the iron.

Zinc-plated or galvanized iron uses a different strategy. Zinc is more easily oxidized than iron because zinc has a lower reduction potential. Since zinc has a lower reduction potential, it is a more active metal. Thus, even if the zinc coating is scratched, the zinc will still oxidize before the iron. This suggests that this approach should work with other active metals.

Figure 9.6.3: One way to protect an underground iron storage tank is through cathodic protection. Using an active metal like zinc or magnesium for the anode effectively makes the storage tank the cathode, preventing it from corroding (oxidizing).

A diagram is shown of an underground storage tank system. Underground, to the left end of the diagram is a horizontal grey tank which is labeled “Object to be protected.” A black line extends upward from the center of the tank above ground. An arrow points upward at the left side of the line segment. A horizontal black line segment continues right above ground, which is labeled “No power source is needed.” A line segment extends up and to the right, which is labeled “ Lead wire.” A line segment with a downward pointing arrow to its right extends downward below the ground to a second metal tank-like structure, labeled “Sacrificial anode” which is vertically oriented. Five black arrows point left underground toward the first tank. These arrows are collectively labeled “Protective current.”

Another important way to protect metal is to make it the cathode in a galvanic cell. This is cathodic protection and can be used for metals other than just iron. For example, the rusting of underground iron storage tanks and pipes can be prevented or greatly reduced by connecting them to a more active metal such as zinc or magnesium. This is also used to protect the metal parts in water heaters. The more active metals (lower reduction potential) are called sacrificial anodes because as they get used up as they corrode (oxidize) at the anode. The metal being protected serves as the cathode, and so does not oxidize (corrode). When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.

Summary

Corrosion is the degradation of a metal caused by an electrochemical process. Large sums of money are spent each year repairing the effects of, or preventing, corrosion. Some metals, such as aluminum and copper, produce a protective layer when they corrode in air. The thin layer that forms on the surface of the metal prevents oxygen from coming into contact with more of the metal atoms and thus “protects” the remaining metal from further corrosion. Iron corrodes (forms rust) when exposed to water and oxygen. The rust that forms on iron metal flakes off, exposing fresh metal, which also corrodes. One way to prevent, or slow, corrosion is by coating the metal. Coating prevents water and oxygen from contacting the metal. Paint or other coatings will slow corrosion, but they are not effective once scratched. Zinc-plated or galvanized iron exploits the fact that zinc is more likely to oxidize than iron. As long as the coating remains, even if scratched, the zinc will oxidize before the iron. Another method for protecting metals is cathodic protection. In this method, an easily oxidized and inexpensive metal, often zinc or magnesium (the sacrificial anode), is electrically connected to the metal that must be protected. The more active metal is the sacrificial anode, and is the anode in a galvanic cell. The "protected" metal is the cathode, and remains unoxidized. One advantage of cathodic protection is that the sacrificial anode can be monitored and replaced if needed.

Glossary

cathodic protection	method of protecting metal by using a sacrificial anode and effectively making the metal that needs protecting the cathode, thus preventing its oxidation
corrosion	degradation of metal through an electrochemical process
galvanized iron	method for protecting iron by covering it with zinc, which will oxidize before the iron; zinc-plated iron
sacrificial anode	more active, inexpensive metal used as the anode in cathodic protection; frequently made from magnesium or zinc

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9.7: Electrolysis

Learning Objectives

- Describe electrolytic cells and their relationship to galvanic cells
- Perform various calculations related to electrolysis

In galvanic cells, chemical energy is converted into electrical energy. The opposite is true for electrolytic cells. In electrolytic cells, electrical energy causes nonspontaneous reactions to occur in a process known as electrolysis. The charging electric barttery shows one such process. Electrical energy is converted into the chemical energy in the battery as it is charged. Once charged, the battery can be used to power the automobile. The same principles are involved in electrolytic cells as in galvanic cells. We will look at three electrolytic cells and the quantitative aspects of electrolysis.

9.7.0.0.1: The Electrolysis of Molten Sodium Chloride

In molten sodium chloride, the ions are free to migrate to the electrodes of an electrolytic cell. A simplified diagram of the cell commercially used to produce sodium metal and chlorine gas is shown in Figure 9.7.1. Sodium is a strong reducing agent and chlorine is used to purify water, and is used in antiseptics and in paper production. The reactions are

$$\text{anode: } 2\,\mathrm{Cl^-}(l) \longrightarrow \mathrm{Cl_2}(g) + 2\,\mathrm{e^-} \quad E^\circ_{\mathrm{Cl_2/Cl^-}} = +1.3\ \mathrm{V} \tag{9.7.1}$$

$$\text{cathode: } \mathrm{Na^+}(l) + \mathrm{e^-} \longrightarrow \mathrm{Na}(l) \quad E^\circ_{\mathrm{Na^+/Na}} = -2.7\ \mathrm{V} \tag{9.7.2}$$

$$\text{overall: } 2\,\mathrm{Na^+}(l) + 2\,\mathrm{Cl^-}(l) \longrightarrow 2\,\mathrm{Na}(l) + \mathrm{Cl_2}(g) \quad E^\circ_{\mathrm{cell}} = -4.0\ \mathrm{V} \tag{9.7.3}$$

The power supply (battery) must supply a minimum of 4 V, but, in practice, the applied voltages are typically higher because of inefficiencies in the process itself.

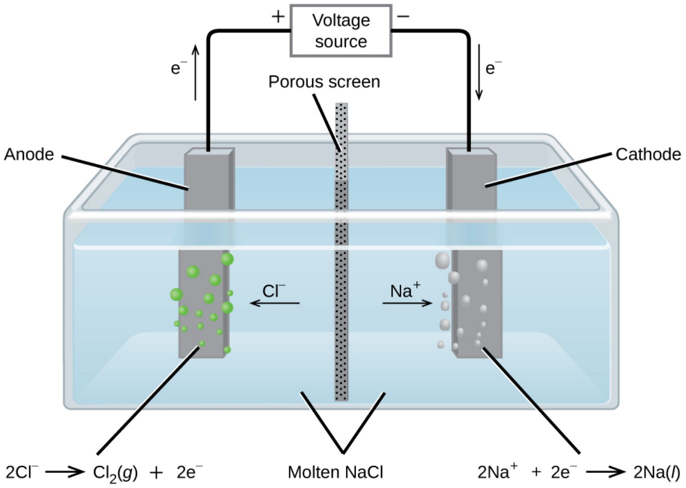

Figure 9.7.1: Passing an electric current through molten sodium chloride decomposes the material into sodium metal and chlorine gas. Care must be taken to keep the products separated to prevent the spontaneous formation of sodium chloride.

9.7.0.0.1: The Electrolysis of Water

It is possible to split water into hydrogen and oxygen gas by electrolysis. Acids are typically added to increase the concentration of hydrogen ion in solution (Figure 9.7.2). The reactions are

$$\text{anode: } 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{O_2}(g) + 4\,\mathrm{H^+}(aq) + 4\,\mathrm{e^-} \quad E^\circ_{\mathrm{anode}} = +1.229\ \mathrm{V} \tag{9.7.4}$$

$$\text{cathode: } 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}(g) \quad E^\circ_{\mathrm{cathode}} = 0\ \mathrm{V} \tag{9.7.5}$$

$$\text{overall: } 2\,\mathrm{H_2O}(l) \longrightarrow 2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \quad E^\circ_{\mathrm{cell}} = -1.229\ \mathrm{V} \tag{9.7.6}$$

Note that the sulfuric acid is not consumed and that the volume of hydrogen gas produced is twice the volume of oxygen gas produced. The minimum applied voltage is 1.229 V.

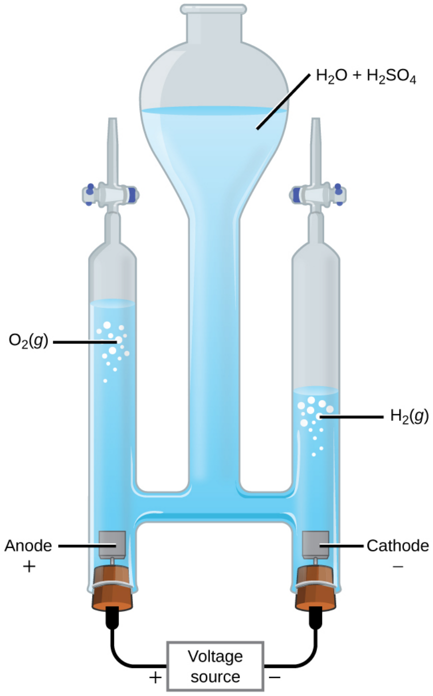

Figure 9.7.2: Water decomposes into oxygen and hydrogen gas during electrolysis. Sulfuric acid was added to increase the concentration of hydrogen ions and the total number of ions in solution, but does not take part in the reaction. The volume of hydrogen gas collected is twice the volume of oxygen gas collected, due to the stoichiometry of the reaction.

9.7.0.0.1: The Electrolysis of Aqueous Sodium Chloride

The electrolysis of aqueous sodium chloride is the more common example of electrolysis because more than one species can be oxidized and reduced. Considering the anode first, the possible reactions are

$$\text{(i) } 2\,\mathrm{Cl^-}(aq) \longrightarrow \mathrm{Cl_2}(g) + 2\,\mathrm{e^-} \qquad E^\circ_{\text{anode}} = +1.35827\text{ V} \tag{9.7.7}$$

$$\text{(ii) } 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{O_2}(g) + 4\,\mathrm{H^+}(aq) + 4\,\mathrm{e^-} \qquad E^\circ_{\text{anode}} = +1.229\text{ V} \tag{9.7.8}$$

These values suggest that water should be oxidized at the anode because a smaller potential would be needed—using reaction (ii) for the oxidation would give a less-negative cell potential. When the experiment is run, it turns out chlorine, not oxygen, is produced at the anode. The unexpected process is so common in electrochemistry that it has been given the name overpotential. The overpotential is the difference between the theoretical cell voltage and the actual voltage that is necessary to cause electrolysis. It turns out that the overpotential for oxygen is rather high and effectively makes the reduction potential more positive. As a result, under normal conditions, chlorine gas is what actually forms at the anode.

Now consider the cathode. Three reductions could occur:

$$\text{(iii) } 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}(g) \qquad E^\circ_{\text{cathode}} = 0\text{ V} \tag{9.7.9}$$

$$\text{(iv) } 2\,\mathrm{H_2O}(l) + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}(g) + 2\,\mathrm{OH^-}(aq) \qquad E^\circ_{\text{cathode}} = -0.8277\text{ V} \tag{9.7.10}$$

$$\text{(v) } \mathrm{Na^+}(aq) + \mathrm{e^-} \longrightarrow \mathrm{Na}(s) \qquad E^\circ_{\text{cathode}} = -2.71\text{ V} \tag{9.7.11}$$

Reaction (v) is ruled out because it has such a negative reduction potential. Under standard state conditions, reaction (iii) would be preferred to reaction (iv). However, the pH of a sodium chloride solution is 7, so the concentration of hydrogen ions is only 1×10^{-7} *M*. At such low concentrations, reaction (iii) is unlikely and reaction (iv) occurs. The overall reaction is then

$$\text{overall: } 2\,\mathrm{H_2O}(l) + 2\,\mathrm{Cl^-}(aq) \longrightarrow \mathrm{H_2}(g) + \mathrm{Cl_2}(g) + 2\,\mathrm{OH^-}(aq) \qquad E^\circ_{\text{cell}} = -2.186\text{ V}$$

As the reaction proceeds, hydroxide ions replace chloride ions in solution. Thus, sodium hydroxide can be obtained by evaporating the water after the electrolysis is complete. Sodium hydroxide is valuable in its own right and is used for things like oven cleaner, drain opener, and in the production of paper, fabrics, and soap.

9.7.0.0.1: Electroplating

An important use for electrolytic cells is in electroplating. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chrome-plated automobile parts, and jewelry. We can get an idea of how this works by investigating how silver-plated tableware is produced (Figure $9.7.3$).

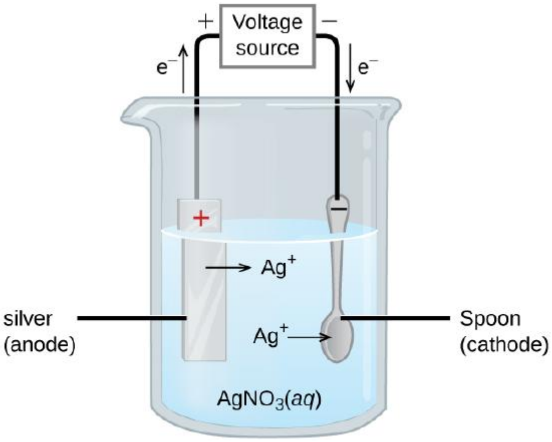

Figure $9.7.3$: The spoon, which is made of an inexpensive metal, is connected to the negative terminal of the voltage source and acts as the cathode. The anode is a silver electrode. Both electrodes are immersed in a silver nitrate solution. When a steady current is passed through the solution, the net result is that silver metal is removed from the anode and deposited on the cathode.

In the figure, the anode consists of a silver electrode, shown on the left. The cathode is located on the right and is the spoon, which is made from inexpensive metal. Both electrodes are immersed in a solution of silver nitrate. As the potential is increased, current flows. Silver metal is lost at the anode as it goes into solution.

$$\text{anode: } \mathrm{Ag}(s) \longrightarrow \mathrm{Ag}^+(aq) + \mathrm{e}^-$$

The mass of the cathode increases as silver ions from the solution are deposited onto the spoon

$$\text{cathode: } \mathrm{Ag}^+(aq) + \mathrm{e}^- \longrightarrow \mathrm{Ag}(s)$$

The net result is the transfer of silver metal from the anode to the cathode. The quality of the object is usually determined by the thickness of the deposited silver and the rate of deposition.

9.7.1: Quantitative Aspects of Electrolysis

The amount of current that is allowed to flow in an electrolytic cell is related to the number of moles of electrons. The number of moles of electrons can be related to the reactants and products using stoichiometry. Recall that the SI unit for current (*I*) is the ampere (A), which is the equivalent of 1 coulomb per second (1 A = 1 $\frac{\mathrm{C}}{\mathrm{s}}$). The total charge (*Q*, in coulombs) is given by

$$Q = I \times t = n \times F$$

where

- *t* is the time in seconds,
- *n* the number of moles of electrons, and
- *F* is the Faraday constant.

Moles of electrons can be used in stoichiometry problems. The time required to deposit a specified amount of metal might also be requested, as in the second of the following examples.

✓ Example 9.7.1: Converting Current to Moles of Electrons

In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

Solution

Faraday's constant can be used to convert the charge (*Q*) into moles of electrons (*n*). The charge is the current (*I*) multiplied by the time

$$n=\frac{Q}{F}=\frac{\frac{10.23\ \mathrm{C}}{\mathrm{s}}\times 1\ \mathrm{hr}\times\frac{60\ \mathrm{min}}{\mathrm{hr}}\times\frac{60\ \mathrm{s}}{\mathrm{min}}}{96,485\ \mathrm{C/mol\ e^-}}=\frac{36,830\ \mathrm{C}}{96,485\ \mathrm{C/mol\ e^-}}=0.3817\ \mathrm{mol\ e^-}$$

From the problem, the solution contains $AgNO_3$, so the reaction at the cathode involves 1 mole of electrons for each mole of silver

$$\text{cathode: } \mathrm{Ag^+}(aq)+\mathrm{e^-}\longrightarrow \mathrm{Ag}(s)$$

The atomic mass of silver is 107.9 g/mol, so

$$\text{mass Ag}=0.3817\ \mathrm{mol\ e^-}\times\frac{1\ \mathrm{mol\ Ag}}{1\ \mathrm{mol\ e^-}}\times\frac{107.9\ \mathrm{g\ Ag}}{1\ \mathrm{mol\ Ag}}=41.19\ \mathrm{g\ Ag}$$

Check your answer: From the stoichiometry, 1 mole of electrons would produce 1 mole of silver. Less than one-half a mole of electrons was involved and less than one-half a mole of silver was produced.

? Exercise 9.7.1

Aluminum metal can be made from aluminum ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of 2.50×10^3 A passed through the solution for 15.0 minutes? Assume the yield is 100%.

Answer

$\mathrm{Al^{3+}}(aq)+3\,\mathrm{e^-}\longrightarrow \mathrm{Al}(s)$; 7.77 mol Al = 210.0 g Al.

✓ Example 9.7.2: Time Required for Deposition

In one application, a 0.010-mm layer of chromium must be deposited on a part with a total surface area of 3.3 m^2 from a solution of containing chromium(III) ions. How long would it take to deposit the layer of chromium if the current was 33.46 A? The density of chromium (metal) is 7.19 g/cm^3.

Solution This problem brings in a number of topics covered earlier. An outline of what needs to be done is:

- If the total charge can be determined, the time required is just the charge divided by the current
- The total charge can be obtained from the amount of Cr needed and the stoichiometry
- The amount of Cr can be obtained using the density and the volume Cr required
- The volume Cr required is the thickness times the area

Solving in steps, and taking care with the units, the volume of Cr required is

$$\text{volume}=\left(0.010\ \mathrm{mm}\times\frac{1\ \mathrm{cm}}{10\ \mathrm{mm}}\right)\times\left(3.3\ \mathrm{m^2}\times\left(\frac{10,000\ \mathrm{cm^2}}{1\ \mathrm{m^2}}\right)\right)=33\ \mathrm{cm^3}$$

Cubic centimeters were used because they match the volume unit used for the density. The amount of Cr is then

$$\text{mass}=\text{volume}\times\text{density}=33\ \cancel{\mathrm{cm^3}}\times\frac{7.19\ \mathrm{g}}{\cancel{\mathrm{cm^3}}}=237\ \mathrm{g\ Cr}$$

$$\text{mol Cr} = 237\text{ g Cr} \times \frac{1\text{ mol Cr}}{52.00\text{ g Cr}} = 4.56\text{ mol Cr}$$

Since the solution contains chromium(III) ions, 3 moles of electrons are required per mole of Cr. The total charge is then

$$Q = 4.56\text{ mol Cr} \times \frac{3\text{ mol e}^-}{1\text{ mol Cr}} \times \frac{96485\text{ C}}{\text{mol e}^-} = 1.32 \times 10^6\text{ C}$$

The time required is then

$$t = \frac{Q}{I} = \frac{1.32 \times 10^6\text{ C}}{33.46\text{ C/s}} = 3.95 \times 10^4\text{ s} = 11.0\text{ hr}$$

Check your answer: In a long problem like this, a single check is probably not enough. Each of the steps gives a reasonable number, so things are probably correct. Pay careful attention to unit conversions and the stoichiometry.

? Exercise 9.7.2

What mass of zinc is required to galvanize the top of a 3.00 m × 5.50 m sheet of iron to a thickness of 0.100 mm of zinc? If the zinc comes from a solution of $Zn(NO_3)_2$ and the current is 25.5 A, how long will it take to galvanize the top of the iron? The density of zinc is 7.140 g/cm^3.

Answer

231 g Zn required 23,000 minutes.

Summary

Using electricity to force a nonspontaneous process to occur is electrolysis. Electrolytic cells are electrochemical cells with negative cell potentials (meaning a positive Gibbs free energy), and so are nonspontaneous. Electrolysis can occur in electrolytic cells by introducing a power supply, which supplies the energy to force the electrons to flow in the nonspontaneous direction. Electrolysis is done in solutions, which contain enough ions so current can flow. If the solution contains only one material, like the electrolysis of molten sodium chloride, it is a simple matter to determine what is oxidized and what is reduced. In more complicated systems, like the electrolysis of aqueous sodium chloride, more than one species can be oxidized or reduced and the standard reduction potentials are used to determine the most likely oxidation (the half-reaction with the largest [most positive] standard reduction potential) and reduction (the half-reaction with the smallest [least positive] standard reduction potential). Sometimes unexpected half-reactions occur because of overpotential. Overpotential is the difference between the theoretical half-reaction reduction potential and the actual voltage required. When present, the applied potential must be increased, making it possible for a different reaction to occur in the electrolytic cell. The total charge, Q, that passes through an electrolytic cell can be expressed as the current (I) multiplied by time ($Q = It$) or as the moles of electrons (n) multiplied by Faraday's constant ($Q = nF$). These relationships can be used to determine things like the amount of material used or generated during electrolysis, how long the reaction must proceed, or what value of the current is required.

Summary

electrolysis

process using electrical energy to cause a nonspontaneous process to occur

electrolytic cell

electrochemical cell in which electrolysis is used; electrochemical cell with negative cell potentials

electroplating

depositing a thin layer of one metal on top of a conducting surface

overpotential

difference between the theoretical potential and actual potential in an electrolytic cell; the "extra" voltage required to make some nonspontaneous electrochemical reaction to occur

9.E: Electrochemistry (Exercises)

Migrated to ADAPT

CHAPTER OVERVIEW

10: Nuclear Chemistry

The chemical reactions that we have considered in previous chapters involve changes in the *electronic* structure of the species involved, that is, the arrangement of the **electrons** around atoms, ions, or molecules. *Nuclear* structure, the numbers of protons and neutrons within the nuclei of the atoms involved, remains unchanged during chemical reactions. This chapter will introduce the topic of nuclear chemistry, which began with the discovery of radioactivity in 1896 by French physicist Antoine Becquerel and has become increasingly important during the twentieth and twenty-first centuries, providing the basis for various technologies related to energy, medicine, geology, and many other areas.

Contributors and Attributions

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10.1: Nuclear Equations

Learning Objectives

- Identify common particles and energies involved in nuclear reactions
- Write and balance nuclear equations

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

10.1.1: Types of Particles in Nuclear Reactions

Many entities can be involved in nuclear reactions. The most common are protons, neutrons, alpha particles, beta particles, positrons, and gamma rays, as shown in Figure 10.1.1. Protons $({}^{1}_{1}\mathrm{p}$, also represented by the symbol ${}^{1}_{1}\mathrm{H})$ and neutrons $({}^{1}_{0}\mathrm{n})$ are the constituents of atomic nuclei, and have been described previously. Alpha particles $({}^{4}_{2}\mathrm{He}$, also represented by the symbol ${}^{4}_{2}\alpha)$ are high-energy helium nuclei. Beta particles $({}^{\;\,0}_{-1}\beta$, also represented by the symbol ${}^{\;\,0}_{-1}\mathrm{e})$ are high-energy electrons, and gamma rays are photons of very high-energy electromagnetic radiation. Positrons $({}^{\;\,0}_{+1}\mathrm{e}$, also represented by the symbol ${}^{\;\,0}_{+1}\beta)$ are positively charged electrons (“anti-electrons”). The subscripts and superscripts are necessary for balancing nuclear equations, but are usually optional in other circumstances. For example, an alpha particle is a helium nucleus (He) with a charge of +2 and a mass number of 4, so it is symbolized ${}^{4}_{2}\mathrm{He}$. This works because, in general, the ion charge is not important in the balancing of nuclear equations.

Figure 10.1.1: Although many species are encountered in nuclear reactions, this table summarizes the names, symbols, representations, and descriptions of the most common of these.

This table has four columns and seven rows. The first row is a header row and it labels each column: “Name,” “Symbol(s),” “Representation,” and “Description.” Under the “Name” column are the following: “Alpha particle,” “Beta particle,” “Positron,” “Proton,” “Neutron,” and “Gamma ray.” Under the “Symbol(s)” column are the following: “ superscript 4 stacked over a subscript 2 H e or lowercase alpha,” “superscript 0 stacked over a subscript 1 e or lowercase beta,” “superscript 0 stacked over a positive subscript 1 e or lowercase beta superscript positive sign,” “superscript 1 stacked over a subscript 1 H or lowercase rho superscript 1 stacked over a subscript 1 H,” “superscript 1 stacked over a subscript 0 n or lowercase eta superscript 1 stacked over a subscript 0 n,” and a lowercase gamma. Under the “Representation column,” are the following: two white sphere attached to two blue spheres of about the same size with positive signs in them; a small red sphere with a negative sign in it; a small red sphere with a positive sign in it; a blue spheres with a positive sign in it; a white sphere; and a purple squiggle ling with an arrow pointing right to a lowercase gamma. Under the “Description” column are the following: “(High-energy) helium nuclei consisting of two protons and two neutrons,” “(High-energy) elections,” “Particles with the same mass as an electron but with 1 unit of positive charge,” “Nuclei of hydrogen atoms,” “Particles with a mass approximately equal to that of a proton but with no charge,” and “Very high-energy electromagnetic radiation.”

Note that positrons are exactly like electrons, except they have the opposite charge. They are the most common example of antimatter, particles with the same mass but the opposite state of another property (for example, charge) than ordinary matter. When antimatter encounters ordinary matter, both are annihilated and their mass is converted into energy in the form of gamma rays (γ)—and other much smaller subnuclear particles, which are beyond the scope of this chapter—according to the mass-energy equivalence equation $E = mc^2$, seen in the preceding section. For example, when a positron and an electron collide, both are annihilated and two gamma ray photons are created:

$${}^{\;\,0}_{-1}\mathrm{e} + {}^{\;\,0}_{+1}\mathrm{e} \rightarrow \gamma + \gamma \tag{10.1.1}$$

Gamma rays compose short wavelength, high-energy electromagnetic radiation and are (much) more energetic than better-known X-rays. Gamma rays are produced when a nucleus undergoes a transition from a higher to a lower energy state, similar to how a photon is produced by an electronic transition from a higher to a lower energy level. Due to the much larger energy differences between nuclear energy shells, gamma rays emanating from a nucleus have energies that are typically millions of times larger than electromagnetic radiation emanating from electronic transitions.

10.1.2: Balancing Nuclear Reactions

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of subatomic particles rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that ${}^{17}_{8}\text{O}$ is a product of the nuclear reaction of ${}^{14}_{7}\text{N}$ and ${}^{4}_{2}\text{He}$ if we knew that a proton, ${}^{1}_{1}\text{H}$, was one of the two products. Example 10.1.1 shows how we can identify a nuclide by balancing the nuclear reaction.

✓ Example 10.1.1: Balancing Equations for Nuclear Reactions

The reaction of an α particle with magnesium-25 $({}^{25}_{12}\text{Mg})$ produces a proton and a nuclide of another element. Identify the new nuclide produced.

Solution

The nuclear reaction can be written as:

$${}^{25}_{12}\text{Mg} + {}^{4}_{2}\text{He} \rightarrow {}^{1}_{1}\text{H} + {}^{\text{A}}_{\text{Z}}\text{X}$$

where

- A is the mass number and
- Z is the atomic number of the new nuclide, X.

Because the sum of the mass numbers of the reactants must equal the sum of the mass numbers of the products:

$$25 + 4 = \text{A} + 1$$

so

$$\text{A} = 28$$

Similarly, the charges must balance, so:

$$12 + 2 = \text{Z} + 1$$

so

$$\text{Z} = 13$$

Check the periodic table: The element with nuclear charge = +13 is aluminum. Thus, the product is ${}^{28}_{13}\text{Al}$.

? Exercise 10.1.1

The nuclide ${}^{125}_{53}\text{I}$ combines with an electron and produces a new nucleus and no other massive particles. What is the equation for this reaction?

Answer

$${}^{125}_{53}\text{I} + {}^{0}_{-1}\text{e} \rightarrow {}^{125}_{52}\text{Te}$$

Following are the equations of several nuclear reactions that have important roles in the history of nuclear chemistry:

- The first naturally occurring unstable element that was isolated, polonium, was discovered by the Polish scientist Marie Curie and her husband Pierre in 1898. It decays, emitting α particles:

$${}^{212}_{84}\text{Po} \longrightarrow {}^{208}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$

- The first nuclide to be prepared by artificial means was an isotope of oxygen, ${}^{17}\text{O}$. It was made by Ernest Rutherford in 1919 by bombarding nitrogen atoms with α particles:

$$^{14}_{7}\text{N} + ^{4}_{2}\alpha \longrightarrow ^{17}_{8}\text{O} + ^{1}_{1}\text{H}$$

- James Chadwick discovered the neutron in 1932, as a previously unknown neutral particle produced along with ^{12}C by the nuclear reaction between ^{9}Be and ^{4}He:

$$^{9}_{4}\text{Be} + ^{4}_{2}\text{He} \longrightarrow ^{12}_{6}\text{C} + ^{1}_{0}\text{n}$$

- The first element to be prepared that does not occur naturally on the earth, technetium, was created by bombardment of molybdenum by deuterons (heavy hydrogen, $^{2}_{1}\text{H}$), by Emilio Segre and Carlo Perrier in 1937:

$$^{2}_{1}\text{H} + ^{97}_{42}\text{Mo} \longrightarrow 2\,^{1}_{0}\text{n} + ^{97}_{43}\text{Tc}$$

- The first controlled nuclear chain reaction was carried out in a reactor at the University of Chicago in 1942. One of the many reactions involved was:

$$^{235}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{87}_{35}\text{Br} + ^{146}_{57}\text{La} + 3\,^{1}_{0}\text{n}$$

Summary

Nuclei can undergo reactions that change their number of protons, number of neutrons, or energy state. Many different particles can be involved in nuclear reactions. The most common are protons, neutrons, positrons (which are positively charged electrons), alpha (α) particles (which are high-energy helium nuclei), beta (β) particles (which are high-energy electrons), and gamma (γ) rays (which compose high-energy electromagnetic radiation). As with chemical reactions, nuclear reactions are always balanced. When a nuclear reaction occurs, the total mass (number) and the total charge remain unchanged.

Glossary

alpha particle

(α or $^{4}_{2}\text{He}$ or $^{4}_{2}\alpha$) high-energy helium nucleus; a helium atom that has lost two electrons and contains two protons and two neutrons

antimatter

particles with the same mass but opposite properties (such as charge) of ordinary particles

beta particle

(β or $^{0}_{-1}\text{e}$ or $^{0}_{-1}\beta$) high-energy electron

gamma ray

(γ or $^{0}_{0}\gamma$) short wavelength, high-energy electromagnetic radiation that exhibits wave-particle duality

nuclear reaction

change to a nucleus resulting in changes in the atomic number, mass number, or energy state

positron ($^{0}_{+1}\beta$ or $^{0}_{+1}\text{e}$)

antiparticle to the electron; it has identical properties to an electron, except for having the opposite (positive) charge

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10.2: Radioactive Decay

Learning Objectives

- Recognize common modes of radioactive decay
- Identify common particles and energies involved in nuclear decay reactions
- Write and balance nuclear decay equations
- Calculate kinetic parameters for decay processes, including half-life
- Describe common radiometric dating techniques

Following the somewhat serendipitous discovery of radioactivity by Becquerel, many prominent scientists began to investigate this new, intriguing phenomenon. Among them were Marie Curie (the first woman to win a Nobel Prize, and the only person to win two Nobel Prizes in different sciences—chemistry and physics), who was the first to coin the term "radioactivity," and Ernest Rutherford (of gold foil experiment fame), who investigated and named three of the most common types of radiation. During the beginning of the twentieth century, many radioactive substances were discovered, the properties of radiation were investigated and quantified, and a solid understanding of radiation and nuclear decay was developed.

The spontaneous change of an unstable nuclide into another is radioactive decay. The unstable nuclide is called the parent nuclide; the nuclide that results from the decay is known as the daughter nuclide. The daughter nuclide may be stable, or it may decay itself. The radiation produced during radioactive decay is such that the daughter nuclide lies closer to the band of stability than the parent nuclide, so the location of a nuclide relative to the band of stability can serve as a guide to the kind of decay it will undergo (Figure 10.2.1).

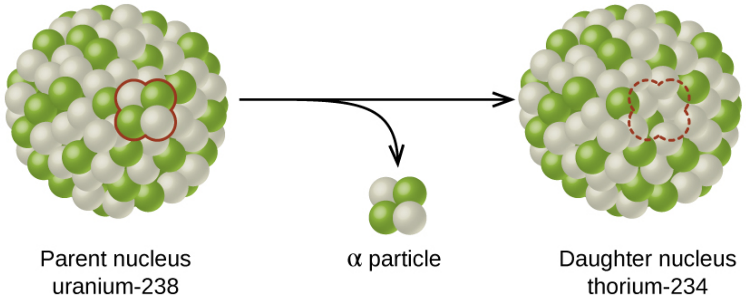


Figure 10.2.1: A nucleus of uranium-238 (the parent nuclide) undergoes α decay to form thorium-234 (the daughter nuclide). The alpha particle removes two protons (green) and two neutrons (gray) from the uranium-238 nucleus.

A diagram shows two spheres composed of many smaller white and green spheres connected by a right-facing arrow with another, down-facing arrow coming off of it. The left sphere, labeled "Parent nucleus uranium dash 238" has two white and two green spheres that are near one another and are outlined in red. These two green and two white spheres are shown near the tip of the down-facing arrow and labeled "alpha particle." The right sphere, labeled "Daughter nucleus radon dash 234," looks the same as the left, but has a space for four smaller spheres outlined with a red dotted line.

Although the radioactive decay of a nucleus is too small to see with the naked eye, we can indirectly view radioactive decay in an environment called a cloud chamber. Click here to learn about cloud chambers and to view an interesting Cloud Chamber Demonstration from the Jefferson Lab.

Video 10.2.1: How to Build a Cloud Chamber!

10.2.1: Types of Radioactive Decay

Ernest Rutherford’s experiments involving the interaction of radiation with a magnetic or electric field (Figure 10.2.2) helped him determine that one type of radiation consisted of positively charged and relatively massive α particles; a second type was made up of negatively charged and much less massive β particles; and a third was uncharged electromagnetic waves, γ rays. We now know that α particles are high-energy helium nuclei, β particles are high-energy electrons, and γ radiation compose high-energy electromagnetic radiation. We classify different types of radioactive decay by the radiation produced.

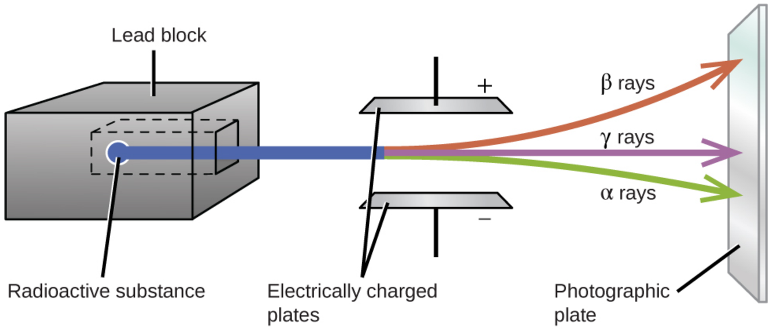


Figure 10.2.2: Alpha particles, which are attracted to the negative plate and deflected by a relatively small amount, must be positively charged and relatively massive. Beta particles, which are attracted to the positive plate and deflected a relatively large amount, must be negatively charged and relatively light. Gamma rays, which are unaffected by the electric field, must be uncharged.

A diagram is shown. A gray box on the left side of the diagram labeled “Lead block” has a chamber hollowed out in the center in which a sample labeled “Radioactive substance” is placed. A blue beam is coming from the sample, out of the block, and passing through two horizontally placed plates that are labeled “Electrically charged plates.” The top plate is labeled with a positive sign while the bottom plate is labeled with a negative sign. The beam is shown to break into three beams as it passes in between the plates; in order from top to bottom, they are red, labeled “beta rays,” purple labeled “gamma rays” and green labeled “alpha rays.” The beams are shown to hit a vertical plate labeled “Photographic plate” on the far right side of the diagram.

Alpha (α) decay is the emission of an α particle from the nucleus. For example, polonium-210 undergoes α decay:

$$^{210}_{84}\mathrm{Po} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{206}_{82}\mathrm{Pb} \qquad \text{or} \qquad ^{210}_{84}\mathrm{Po} \longrightarrow {}^{4}_{2}\alpha + {}^{206}_{82}\mathrm{Pb}$$

Alpha decay occurs primarily in heavy nuclei (A > 200, Z > 83). Because the loss of an α particle gives a daughter nuclide with a mass number four units smaller and an atomic number two units smaller than those of the parent nuclide, the daughter nuclide has a larger n:p ratio than the parent nuclide. If the parent nuclide undergoing α decay lies below **the band of stability**, the daughter nuclide will lie closer to the band.

Beta (β) decay is the emission of an electron from a nucleus. Iodine-131 is an example of a nuclide that undergoes β decay:

$$^{131}_{53}\mathrm{I} \longrightarrow {}^{0}_{-1}\mathrm{e} + {}^{131}_{54}\mathrm{X} \qquad \text{or} \qquad ^{131}_{53}\mathrm{I} \longrightarrow {}^{0}_{-1}\beta + {}^{131}_{54}\mathrm{Xe}$$

Beta decay, which can be thought of as the conversion of a neutron into a proton and a β particle, is observed in nuclides with a large n:p ratio. The beta particle (electron) emitted is from the atomic nucleus and is not one of the electrons surrounding the nucleus. Such nuclei lie above the band of stability. Emission of an electron does not change the mass number of the nuclide but does increase the number of its protons and decrease the number of its neutrons. Consequently, the n:p ratio is decreased, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Gamma emission (γ emission) is observed when a nuclide is formed in an excited state and then decays to its ground state with the emission of a γ ray, a quantum of high-energy electromagnetic radiation. The presence of a nucleus in an excited state is often indicated by an asterisk (*). Cobalt-60 emits γ radiation and is used in many applications including cancer treatment:

$$^{60}_{27}\mathrm{Co}^* \longrightarrow {}^{0}_{0}\gamma + {}^{60}_{27}\mathrm{Co}$$

There is no change in mass number or atomic number during the emission of a γ ray unless the γ emission accompanies one of the other modes of decay.

Positron emission (β^+ decay) is the emission of a positron from the nucleus. Oxygen-15 is an example of a nuclide that undergoes positron emission:

$$^{15}_{8}\mathrm{O} \longrightarrow {}^{0}_{+1}\mathrm{e} + {}^{15}_{7}\mathrm{N} \qquad \text{or} \qquad {}^{15}_{8}\mathrm{O} \longrightarrow {}^{0}_{+1}\beta + {}^{15}_{7}\mathrm{N}$$

Positron emission is observed for nuclides in which the n:p ratio is low. These nuclides lie below the band of stability. Positron decay is the conversion of a proton into a neutron with the emission of a positron. The n:p ratio increases, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Electron capture occurs when one of the inner electrons in an atom is captured by the atom’s nucleus. For example, potassium-40 undergoes electron capture:

$$^{40}_{19}\mathrm{K} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{40}_{18}\mathrm{Ar}$$

Electron capture occurs when an inner shell electron combines with a proton and is converted into a neutron. The loss of an inner shell electron leaves a vacancy that will be filled by one of the outer electrons. As the outer electron drops into the vacancy, it will emit energy. In most cases, the energy emitted will be in the form of an X-ray. Like positron emission, electron capture occurs for “proton-rich” nuclei that lie below the band of stability. Electron capture has the same effect on the nucleus as does positron emission: The atomic number is decreased by one and the mass number does not change. This increases the n:p ratio, and the daughter nuclide lies closer to the band of stability than did the parent nuclide. Whether electron capture or positron emission occurs is difficult to predict. The choice is primarily due to kinetic factors, with the one requiring the smaller activation energy being the one more likely to occur. Figure $10.2.3$ summarizes these types of decay, along with their equations and changes in atomic and mass numbers.

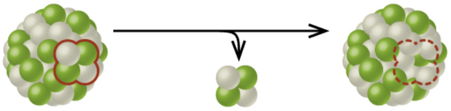
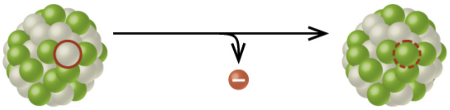
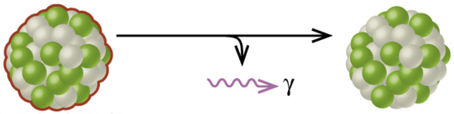
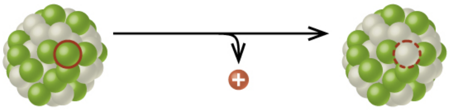
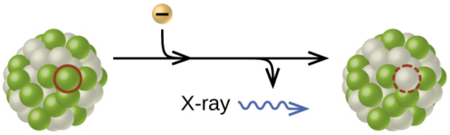
Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	$^{A}_{Z}X \qquad ^{4}_{2}He + ^{A-4}_{Z-2}Y$		A: decrease by 4 Z: decrease by 2
Beta decay	$^{A}_{Z}X \qquad ^{0}_{-1}e + ^{A}_{Z+1}Y$		A: unchanged Z: increase by 1
Gamma decay	$^{A}_{Z}X \qquad ^{0}_{0}\gamma + ^{A}_{Z}Y$	 Excited nuclear state	A: unchanged Z: unchanged
Positron emission	$^{A}_{Z}X \qquad ^{0}_{+1}e + ^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1
Electron capture	$^{A}_{Z}X \qquad ^{0}_{-1}e + ^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1

Figure 10.2.3: This table summarizes the type, nuclear equation, representation, and any changes in the mass or atomic numbers for various types of decay.

This table has four columns and six rows. The first row is a header row and it labels each column: “Type,” “Nuclear equation,” “Representation,” and “Change in mass / atomic numbers.” Under the “Type” column are the following: “Alpha decay,” “Beta decay,” “Gamma decay,” “Positron emission,” and “Electron capture.” Under the “Nuclear equation” column are several equations. Each begins with superscript A stacked over subscript Z X. There is a large gap of space and then the following equations: “superscript 4 stacked over subscript 2 He plus superscript A minus 4 stacked over subscript Z minus 2 Y,” “superscript 0 stacked over subscript negative 1 e plus superscript A stacked over subscript Z plus 1 Y,” “superscript 0 stacked over subscript 0 lowercase gamma plus superscript A stacked over subscript Z Y,” “superscript 0 stacked over subscript positive 1 e plus superscript A stacked over subscript Y minus 1 Y,” and “superscript 0 stacked over subscript negative 1 e plus superscript A stacked over subscript Y minus 1 Y.” Under the “Representation” column are the five diagrams. The first shows a cluster of green and white spheres. A section of the cluster containing two white and two green spheres is outlined. There is a right-facing arrow pointing to a similar cluster as previously described, but the outlined section is missing. From the arrow another arrow branches off and points downward. The small cluster to two white spheres and two green spheres appear at the end of the arrow. The next diagram shows the same cluster of white and green spheres. One white sphere is outlined. There is a right-facing arrow to a similar cluster, but the white sphere is missing. Another arrow branches off the main arrow and a red sphere with a negative sign appears at the end. The next diagram shows the same cluster of white and green spheres. The whole sphere is outlined and labeled, “excited nuclear state.” There is a right-facing arrow that points to the same cluster. No spheres are missing. Off the main arrow is another arrow which points to a purple squiggle arrow which in turn points to a lowercase gamma. The next diagram shows the same cluster of white and green spheres. One green sphere is outlined. There is a right-facing arrow to a similar cluster, but the green sphere is missing. Another arrow branches off the main arrow and a red sphere with a positive sign appears at the end. The next diagram shows the same cluster of white and green spheres. One green sphere is outlined. There is a right-facing arrow to a similar cluster, but the green sphere is missing. Two other arrows branch off the main arrow. The first shows a gold sphere with a negative sign joining with the right-facing arrow. The secon points to a blue squiggle arrow labeled, “X-ray.” Under the “Change in mass / atomic numbers” column are the following: “A: decrease by 4, Z: decrease by 2,” “A: unchanged, Z: increased by 1,” “A: unchanged, Z: unchanged,” “A: unchanged, Z: unchanged,” “A: unchanged, Z: decrease by 1,” and “A: unchanged, Z: decrease by 1.”

PET Scan

Positron emission tomography (PET) scans use radiation to diagnose and track health conditions and monitor medical treatments by revealing how parts of a patient’s body function (Figure 10.2.4). To perform a PET scan, a positron-emitting radioisotope is produced in a cyclotron and then attached to a substance that is used by the part of the body being investigated. This “tagged” compound, or radiotracer, is then put into the patient (injected via IV or breathed in as a gas), and how it is used by the tissue reveals how that organ or other area of the body functions.

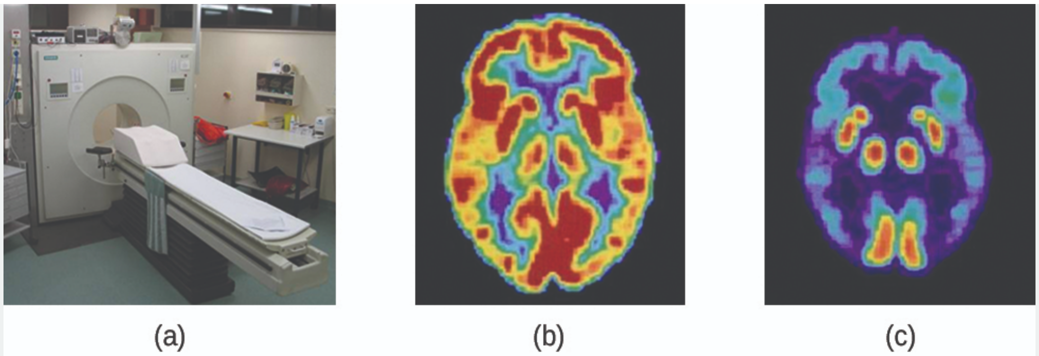


Figure 10.2.4: A PET scanner (a) uses radiation to provide an image of how part of a patient's body functions. The scans it produces can be used to image a healthy brain (b) or can be used for diagnosing medical conditions such as Alzheimer's disease (c). (credit a: modification of work by Jens Maus)

Three pictures are shown and labeled "a," "b" and "c." Picture a shows a machine with a round opening connected to an examination table. Picture b is a medical scan of the top of a person's head and shows large patches of yellow and red and smaller patches of blue, green and purple highlighting. Picture c also shows a medical scan of the top of a person's head, but this image is mostly colored in blue and purple with very small patches of red and yellow.

For example, F-18 is produced by proton bombardment of $^{18}\mathrm{O}$ $\left({}^{18}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{p} \longrightarrow {}^{18}_{9}\mathrm{F} + {}^{1}_{0}\mathrm{n}\right)$ and incorporated into a glucose analog called fludeoxyglucose (FDG). How FDG is used by the body provides critical diagnostic information; for example, since cancers use glucose differently than normal tissues, FDG can reveal cancers. The $^{18}\mathrm{F}$ emits positrons that interact with nearby electrons, producing a burst of gamma radiation. This energy is detected by the scanner and converted into a detailed, three-dimensional, color image that shows how that part of the patient's body functions. Different levels of gamma radiation produce different amounts of brightness and colors in the image, which can then be interpreted by a radiologist to reveal what is going on. PET scans can detect heart damage and heart disease, help diagnose Alzheimer's disease, indicate the part of a brain that is affected by epilepsy, reveal cancer, show what stage it is, and how much it has spread, and whether treatments are effective. Unlike magnetic resonance imaging and X-rays, which only show how something looks, the big advantage of PET scans is that they show how something functions. PET scans are now usually performed in conjunction with a computed tomography scan.

10.2.2: Radioactive Decay Series

The naturally occurring radioactive isotopes of the heaviest elements fall into chains of successive disintegrations, or decays, and all the species in one chain constitute a radioactive family, or radioactive decay series. Three of these series include most of the naturally radioactive elements of the periodic table. They are the uranium series, the actinide series, and the thorium series. The neptunium series is a fourth series, which is no longer significant on the earth because of the short half-lives of the species involved. Each series is characterized by a parent (first member) that has a long half-life and a series of daughter nuclides that ultimately lead to a stable end-product—that is, a nuclide on the band of stability (Figure $10.2.5$). In all three series, the end-product is a stable isotope of lead. The neptunium series, previously thought to terminate with bismuth-209, terminates with thallium-205.

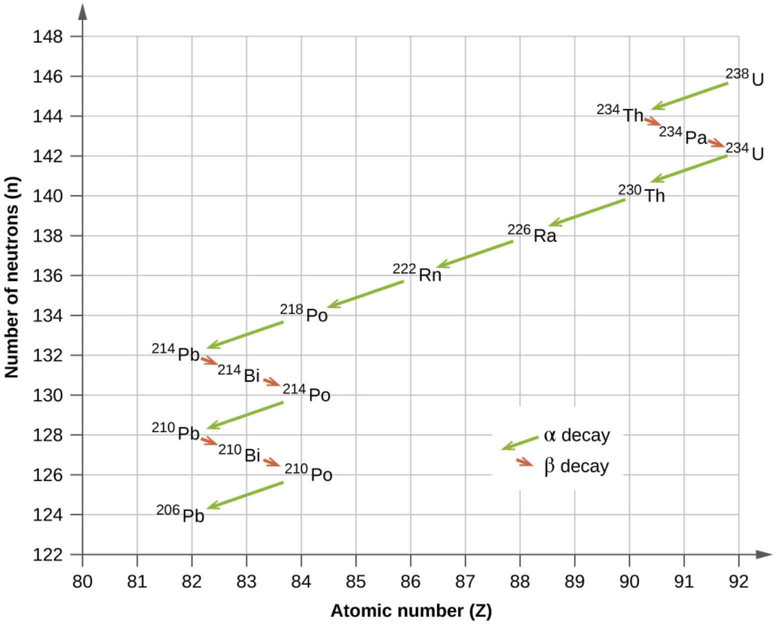


Figure 10.2.5: Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight α decays and six β decays.

A graph is shown where the x-axis is labeled “Number of neutrons, open parenthesis, n, close parenthesis” and has values of 122 to 148 in increments of 2. The y-axis is labeled “Atomic number” and has values of 80 to 92 in increments of 1. Two types of arrows are used in this graph to connect the points. Green arrows are labeled as “alpha decay” while red arrows are labeled “beta decay.” Beginning at the point “92, 146” that is labeled “superscript 238, U,” a green arrow connects this point to the second point “90, 144” which is labeled “superscript 234, T h.” A red arrow connect this to the third point “91, 143” which is labeled “superscript 234, P a” which is connected to the fourth point “92, 142” by a red arrow and which is labeled “superscript 234, U.” A green arrow leads to the next point, “90, 140” which is labeled “superscript 230, T h” and is connected by a green arrow to the sixth point, “88, 138” which is labeled “superscript 226, R a” that is in turn connected by a green arrow to the seventh point “86, 136” which is labeled “superscript 222, Ra.” The eighth point, at “84, 134” is labeled “superscript 218, P o” and has green arrows leading to it and away from it to the ninth point “82, 132” which is labeled “superscript 214, Pb” which is connected by a red arrow to the tenth point, “83, 131” which is labeled “superscript 214, B i.” A red arrow leads to the eleventh point “84, 130” which is labeled “superscript 214, P o” and a green arrow leads to the twelvth point “82, 128” which is labeled “superscript 210, P b.” A red arrow leads to the thirteenth point “83, 127” which is labeled “superscript 210, B i” and a red arrow leads to the fourteenth point “84, 126” which is labeled “superscript 210, P o.” The final point is labeled “82, 124” and “superscript 206, P b.”

10.2.3: Radioactive Half-Lives

Radioactive decay follows first-order kinetics. Since first-order reactions have already been covered in detail in the kinetics chapter, we will now apply those concepts to nuclear decay reactions. Each radioactive nuclide has a characteristic, constant half-life ($t_{1/2}$), the time required for half of the atoms in a sample to decay. An isotope’s half-life allows us to determine how long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, cobalt-60, an isotope that emits gamma rays used to treat cancer, has a half-life of 5.27 years (Figure 10.2.6). In a given cobalt-60 source, since half of the $^{60}_{27}\text{Co}$ nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

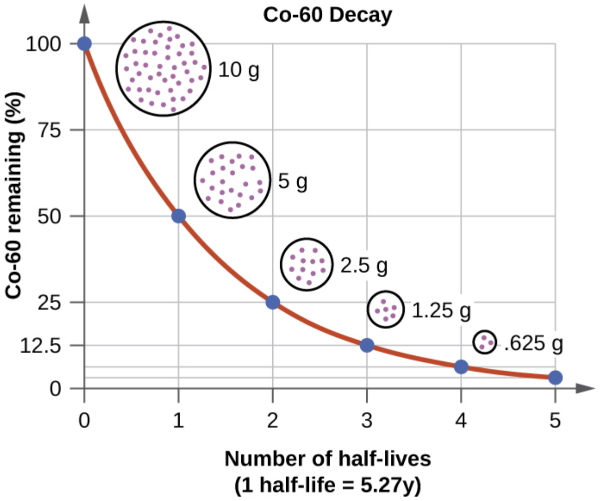


Figure 10.2.6: For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

A graph, titled “C o dash 60 Decay,” is shown where the x-axis is labeled “C o dash 60 remaining, open parenthesis, percent sign, close parenthesis” and has values of 0 to 100 in increments of 25. The y-axis is labeled “Number of half dash lives” and has values of 0 to 5 in increments of 1. The first point, at “0, 100” has a circle filled with tiny dots drawn near it labeled “10 g.” The second point, at “1, 50” has a smaller circle filled with tiny dots drawn near it labeled “5 g.” The third point, at “2, 25” has a small circle filled with tiny dots drawn near it labeled “2.5 g.” The fourth point, at “3, 12.5” has a very small circle filled with tiny dots drawn near it labeled “1.25 g.” The last point, at “4, 6.35” has a tiny circle filled with tiny dots drawn near it labeled.”625 g.”

Since nuclear decay follows first-order kinetics, we can adapt the mathematical relationships used for first-order chemical reactions. We generally substitute the number of nuclei, *N*, for the concentration. If the rate is stated in nuclear decays per second, we refer to it as the activity of the radioactive sample. The rate for radioactive decay is:

$$\text{decay rate} = \lambda N$$

with λ is the **decay constant** for the particular radioisotope.

The decay constant, λ, which is the same as a rate constant discussed in the kinetics chapter. It is possible to express the decay constant in terms of the half-life, $t_{1/2}$:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}} \qquad \text{or} \qquad t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

The first-order equations relating amount, *N*, and time are:

$$N_t = N_0 e^{-kt} \qquad \text{or} \qquad t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right)$$

where N_0 is the initial number of nuclei or moles of the isotope, and N_t is the number of nuclei/moles remaining at time *t*. Example $10.2.1$ applies these calculations to find the rates of radioactive decay for specific nuclides.

✓ Example 10.2.1: Rates of Radioactive Decay

$^{60}_{27}\text{Co}$ decays with a half-life of 5.27 years to produce $^{60}_{28}\text{Ni}$.

a. What is the decay constant for the radioactive disintegration of cobalt-60?
b. Calculate the fraction of a sample of the $^{60}_{27}\text{Co}$ isotope that will remain after 15 years.
c. How long does it take for a sample of $^{60}_{27}\text{Co}$ to disintegrate to the extent that only 2.0% of the original amount remains?

Solution

(a) The value of the rate constant is given by:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5.27\text{ y}} = 0.132\text{ y}^{-1}$$

(b) The fraction of $^{60}_{27}\text{Co}$ that is left after time t is given by $\frac{N_t}{N_0}$. Rearranging the first-order relationship $N_t = N_0e^{-\lambda t}$ to solve for this ratio yields:

$$\frac{N_t}{N_0} = e^{-\lambda t} = e^{-(0.132/\text{y})(15.0/\text{y})} = 0.138$$

The fraction of $^{60}_{27}\text{Co}$ that will remain after 15.0 years is 0.138. Or put another way, 13.8% of the $^{60}_{27}\text{Co}$ originally present will remain after 15 years.

(c) 2.00% of the original amount of $^{60}_{27}\text{Co}$ is equal to $0.0200 \times N_0$. Substituting this into the equation for time for first-order kinetics, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) = -\frac{1}{0.132\ \text{y}^{-1}}\ln\left(\frac{0.0200 \times N_0}{N_0}\right) = 29.6\ \text{y}$$

Exercise 10.2.1

Radon-222, $^{222}_{86}\text{Rn}$, has a half-life of 3.823 days. How long will it take a sample of radon-222 with a mass of 0.750 g to decay into other elements, leaving only 0.100 g of radon-222?

Answer

11.1 days

Because each nuclide has a specific number of nucleons, a particular balance of repulsion and attraction, and its own degree of stability, the half-lives of radioactive nuclides vary widely. For example: the half-life of $^{209}_{83}\text{Bi}$ is 1.9×10^{19} years; $^{239}_{94}\text{Ra}$ is 24,000 years; $^{222}_{86}\text{Rn}$ is 3.82 days; and element-111 (Rg for roentgenium) is 1.5×10^{-3} seconds. The half-lives of a number of radioactive isotopes important to medicine are shown in Table $10.2.1$, and others are listed in Appendix N1.

Table 10.2.1: Half-lives of Radioactive Isotopes Important to Medicine

Type	Decay Mode	Half-Life	Uses
F-18	β^+ decay	110. minutes	PET scans
Co-60	β decay, γ decay	5.27 years	cancer treatment
Tc-99m[1]	γ decay	8.01 hours	scans of brain, lung, heart, bone
I-131	β decay	8.02 days	thyroid scans and treatment
Tl-201	electron capture	73 hours	heart and arteries scans; cardiac stress tests

The “m” in Tc-99m stands for “metastable,” indicating that this is an unstable, high-energy state of Tc-99. Metastable isotopes emit γ radiation to rid themselves of excess energy and become (more) stable.

10.2.4: Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of “dating” the origin of objects such as archaeological artifacts, formerly living organisms, or geological formations. This process is radiometric dating and has been responsible for many breakthrough scientific discoveries about the geological history of the earth, the evolution of life, and the history of human civilization. We will explore some of the most common types of radioactive dating and how the particular isotopes work for each type.

10.2.4.1: Radioactive Dating Using Carbon-14

The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called radiocarbon dating or carbon-14 dating, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes: ${}^{12}_{6}\mathrm{C}$, which constitutes about 99% of the carbon on earth; ${}^{13}_{6}\mathrm{C}$, about 1% of the total; and trace amounts of ${}^{14}_{6}\mathrm{C}$. Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:

$$ {}^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} $$

All isotopes of carbon react with oxygen to produce CO_2 molecules. The ratio of ${}^{14}_{6}\mathrm{CO}_2$ to ${}^{12}_{6}\mathrm{CO}_2$ depends on the ratio of ${}^{14}_{6}\mathrm{CO}$ to ${}^{12}_{6}\mathrm{CO}$ in the atmosphere. The natural abundance of ${}^{14}_{6}\mathrm{CO}$ in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen is gas samples found trapped in ice. The incorporation of ${}^{14}_{6}\mathrm{C}{}^{14}_{6}\mathrm{CO}_2$ and ${}^{12}_{6}\mathrm{CO}_2$ into plants is a regular part of the photosynthesis process, which means that the ${}^{14}_{6}\mathrm{C} : {}^{12}_{6}\mathrm{C}$ ratio found in a living plant is the same as the ${}^{14}_{6}\mathrm{C} : {}^{12}_{6}\mathrm{C}$ ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because ${}^{12}_{6}\mathrm{C}$ is a stable isotope and does not undergo radioactive decay, its concentration in the plant does not change. However, carbon-14 decays by β emission with a half-life of 5730 years:

$$ {}^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e} $$

Thus, the ${}^{14}_{6}\mathrm{C} : {}^{12}_{6}\mathrm{C}$ ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant). Figure $10.2.7$ visually depicts this process.

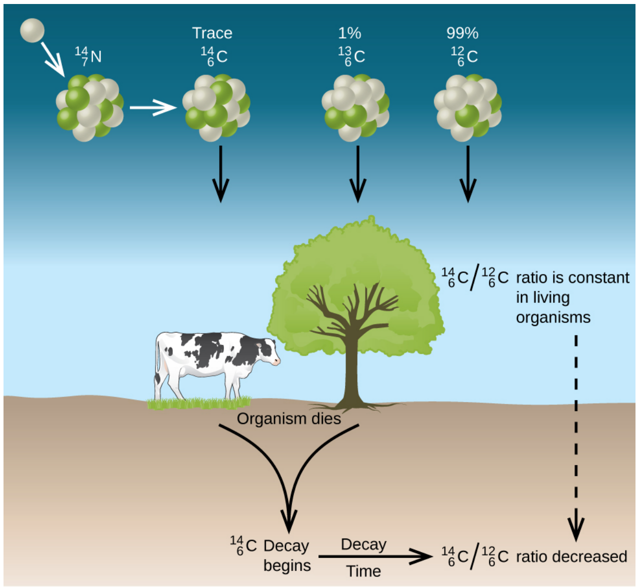


Figure $10.2.7$: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died).

A diagram shows a cow standing on the ground next to a tree. In the upper left of the diagram, where the sky is represented, a single white sphere is shown and is connected by a downward-facing arrow to a larger sphere composed of green and white spheres that is labeled “superscript 14, subscript 7, N.” This structure is connected to three other structures by a right-facing arrow. Each of the three it points to are composed of green and white spheres and all have arrows pointing from them to the ground. The first of these is labeled “Trace, superscript 14, subscript 6, C,” the second is labeled “1 percent, superscript 13, subscript 6, C” and the last is labeled “99 percent, superscript 12, subscript 6, C.” Two downward-facing arrows that merge into one arrow lead from the cow and tree to the ground and are labeled “organism dies” and “superscript 14, subscript 6, C, decay begins.” A right-facing arrow labeled on top as “Decay” and on bottom as “Time” leads from this to a label of “superscript 14, subscript 6, C, backslash, superscript 12, subscript 6, C, ratio decreased.” Near the top of the tree is a downward facing arrow with the label “superscript 14, subscript 6, C, backslash, superscript 12, subscript 6, C, ratio is constant in living organisms” that leads to the last of the lower statements.

For example, with the half-life of ${}^{14}_{6}\mathrm{C}$ being 5730 years, if the ${}^{14}_{6}\mathrm{C} : {}^{12}_{6}\mathrm{C}$ ratio in a wooden object found in an archaeological dig is half what it is in a living tree, this indicates that the wooden object is 5730 years old. Highly accurate determinations of ${}^{14}_{6}\mathrm{C} : {}^{12}_{6}\mathrm{C}$ ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

Example 10.2.2: Radiocarbon Dating

A tiny piece of paper (produced from formerly living plant matter) taken from the Dead Sea Scrolls has an activity of 10.8 disintegrations per minute per gram of carbon. If the initial C-14 activity was 13.6 disintegrations/min/g of C, estimate the age of the Dead Sea Scrolls.

Solution

The rate of decay (number of disintegrations/minute/gram of carbon) is proportional to the amount of radioactive C-14 left in the paper, so we can substitute the rates for the amounts, *N*, in the relationship:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) \longrightarrow t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_t}{\text{Rate}_0}\right)$$

where the subscript 0 represents the time when the plants were cut to make the paper, and the subscript *t* represents the current time.

The decay constant can be determined from the half-life of C-14, 5730 years:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5730 \text{ y}} = 1.21 \times 10^{-4} \text{ y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_t}{\text{Rate}_0}\right) = -\frac{1}{1.21 \times 10^{-4} \text{ y}^{-1}}\ln\left(\frac{10.8 \text{ dis/min/g C}}{13.6 \text{ dis/min/g C}}\right) = 1910 \text{ y}$$

Therefore, the Dead Sea Scrolls are approximately 1900 years old (Figure 10.2.8).

Figure 10.2.8: Carbon-14 dating has shown that these pages from the Dead Sea Scrolls were written or copied on paper made from plants that died between 100 BC and AD 50.

Exercise 10.2.2

More accurate dates of the reigns of ancient Egyptian pharaohs have been determined recently using plants that were preserved in their tombs. Samples of seeds and plant matter from King Tutankhamun's tomb have a C-14 decay rate of 9.07 disintegrations/min/g of C. How long ago did King Tut's reign come to an end?

Answer

about 3350 years ago, or approximately 1340 BC

There have been some significant, well-documented changes to the ${}^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ ratio. The accuracy of a straightforward application of this technique depends on the ${}^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ ratio in a living plant being the same now as it was in an earlier era, but this is not always valid. Due to the increasing accumulation of CO_2 molecules (largely ${}^{12}_{6}\text{CO}_2$) in the atmosphere caused by combustion of fossil fuels (in which essentially all of the ${}^{14}_{6}\text{C}$ has decayed), the ratio of ${}^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ in the atmosphere may be changing. This manmade increase in ${}^{12}_{6}\text{CO}_2$ in the atmosphere causes the ${}^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ ratio to decrease, and this in turn affects the ratio in currently living organisms on the earth. Fortunately, however, we can use other data, such as tree dating via examination of annual growth rings, to calculate correction factors. With these correction factors, accurate dates can be determined. In general, radioactive dating only works for about 10 half-lives; therefore, the limit for carbon-14 dating is about 57,000 years.

10.2.4.2: Radioactive Dating Using Nuclides Other than Carbon-14

Radioactive dating can also use other radioactive nuclides with longer half-lives to date older events. For example, uranium-238 (which decays in a series of steps into lead-206) can be used for establishing the age of rocks (and the approximate age of the oldest rocks on earth). Since U-238 has a half-life of 4.5 billion years, it takes that amount of time for half of the original U-238 to decay into Pb-206. In a sample of rock that does not contain appreciable amounts of Pb-208, the most abundant isotope of lead, we can assume that lead was not present when the rock was formed. Therefore, by measuring and analyzing the ratio of U-238:Pb-206, we can determine the age of the rock. This assumes that all of the lead-206 present came from the decay of uranium-238. If there is additional lead-206 present, which is indicated by the presence of other lead isotopes in the sample, it is necessary to make an adjustment. Potassium-argon dating uses a similar method. K-40 decays by positron emission and electron capture to form Ar-40 with a half-life of 1.25 billion years. If a rock sample is crushed and the amount of Ar-40 gas that escapes is measured, determination of the Ar-40:K-40 ratio yields the age of the rock. Other methods, such as rubidium-strontium dating (Rb-87 decays into Sr-87 with a half-life of 48.8 billion years), operate on the same principle. To estimate the lower limit for the earth's age, scientists determine the age of various rocks and minerals, making the assumption that the earth is older than the oldest rocks and minerals in its crust. As of 2014, the oldest known rocks on earth are the Jack Hills zircons from Australia, found by uranium-lead dating to be almost 4.4 billion years old.

✓ Example 10.2.3: Radioactive Dating of Rocks

An igneous rock contains 9.58×10^{-5} g of U-238 and 2.51×10^{-5} g of Pb-206, and much, much smaller amounts of Pb-208. Determine the approximate time at which the rock formed.

Solution

The sample of rock contains very little Pb-208, the most common isotope of lead, so we can safely assume that all the Pb-206 in the rock was produced by the radioactive decay of U-238. When the rock formed, it contained all of the U-238 currently in it, plus some U-238 that has since undergone radioactive decay.

The amount of U-238 currently in the rock is:

$$9.58 \times 10^{-5}\ \text{g}\ \cancel{\text{U}} \times \left(\frac{1\ \text{mol U}}{238\ \text{g}\ \cancel{\text{U}}}\right) = 4.03 \times 10^{-7}\ \text{mol U}$$

Because when one mole of U-238 decays, it produces one mole of Pb-206, the amount of U-238 that has undergone radioactive decay since the rock was formed is:

$$2.51 \times 10^{-5}\ \text{g}\ \cancel{\text{Pb}} \times \left(\frac{1\ \text{mol}\ \cancel{\text{Pb}}}{206\ \text{g}\ \cancel{\text{Pb}}}\right) \times \left(\frac{1\ \text{mol U}}{1\ \text{mol}\ \cancel{\text{Pb}}}\right) = 1.22 \times 10^{-7}\ \text{mol U}$$

The total amount of U-238 originally present in the rock is therefore:

$$4.03 \times 10^{-7}\ \text{mol} + 1.22 \times 10^{-7}\ \text{mol} = 5.25 \times 10^{-7}\ \text{mol U}$$

The amount of time that has passed since the formation of the rock is given by:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right)$$

with N_0 representing the original amount of U-238 and N_t representing the present amount of U-238.

U-238 decays into Pb-206 with a half-life of 4.5×10^9 y, so the decay constant λ is:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9\ \text{y}} = 1.54 \times 10^{-10}\ \text{y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{1.54 \times 10^{-10}\ \text{y}^{-1}}\ln\left(\frac{4.03 \times 10^{-7}\ \text{mol}\ \cancel{\text{U}}}{5.25 \times 10^{-7}\ \text{mol}\ \cancel{\text{U}}}\right) = 1.7 \times 10^9\ \text{y}$$

Therefore, the rock is approximately 1.7 billion years old.

? Exercise 10.2.3

A sample of rock contains 6.14 × 10^{-4} g of Rb-87 and 3.51 × 10^{-5} g of Sr-87. Calculate the age of the rock. (The half-life of the β decay of Rb-87 is 4.7 × 10^{10} y.)

Answer

3.7 × 10^9 y

Summary

Nuclei that have unstable n:p ratios undergo spontaneous radioactive decay. The most common types of radioactivity are α decay, β decay, γ emission, positron emission, and electron capture. Nuclear reactions also often involve γ rays, and some nuclei decay by electron capture. Each of these modes of decay leads to the formation of a new nucleus with a more stable n:p ratio. Some substances undergo radioactive decay series, proceeding through multiple decays before ending in a stable isotope. All nuclear decay processes follow first-order kinetics, and each radioisotope has its own characteristic half-life, the time that is required for half of its atoms to decay. Because of the large differences in stability among nuclides, there is a very wide range of half-lives of radioactive substances. Many of these substances have found useful applications in medical diagnosis and treatment, determining the age of archaeological and geological objects, and more.

10.2.5: Key Equations

- decay rate = λN
- $t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$

Glossary

alpha (α) decay

loss of an alpha particle during radioactive decay

beta (β) decay

breakdown of a neutron into a proton, which remains in the nucleus, and an electron, which is emitted as a beta particle

daughter nuclide

nuclide produced by the radioactive decay of another nuclide; may be stable or may decay further

electron capture

combination of a core electron with a proton to yield a neutron within the nucleus

gamma (γ) emission

decay of an excited-state nuclide accompanied by emission of a gamma ray

half-life ($t_{1/2}$)

time required for half of the atoms in a radioactive sample to decay

parent nuclide

unstable nuclide that changes spontaneously into another (daughter) nuclide

positron emission

(also, β^+ decay) conversion of a proton into a neutron, which remains in the nucleus, and a positron, which is emitted

radioactive decay

spontaneous decay of an unstable nuclide into another nuclide

radioactive decay series

chains of successive disintegrations (radioactive decays) that ultimately lead to a stable end-product

radiocarbon dating

highly accurate means of dating objects 30,000–50,000 years old that were derived from once-living matter; achieved by calculating the ratio of $^{14}_{6}\text{C} : ^{12}_{6}\text{C}$ in the object vs. the ratio of $^{14}_{6}\text{C} : ^{12}_{6}\text{C}$ in the present-day atmosphere

radiometric dating

use of radioisotopes and their properties to date the formation of objects such as archeological artifacts, formerly living organisms, or geological formations

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10.3: Nuclear Structure and Stability

Learning Objectives

- Describe nuclear structure in terms of protons, neutrons, and electrons
- Calculate mass defect and binding energy for nuclei
- Explain trends in the relative stability of nuclei

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of $^{1}_{1}\mathrm{H}$, neutrons. Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term nuclide and identify it by the notation:

$$^{\mathrm{A}}_{\mathrm{Z}}\mathrm{X} \tag{10.3.1}$$

where

- X is the symbol for the element,
- A is the mass number, and
- Z is the atomic number.

Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, $^{14}_{6}\mathrm{C}$ is called "carbon-14."

Protons and neutrons, collectively called nucleons, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8×10^{14} grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of 22.6 g/cm^3. If the earth's density were equal to the average nuclear density, the earth's radius would be only about 200 meters (earth's actual radius is approximately 6.4×10^6 meters, 30,000 times larger). Example $10.3.1$ demonstrates just how great nuclear densities can be in the natural world.

Example 10.3.1: Neutron Stars

Density of a Neutron Star Neutron stars form when the core of a very massive star undergoes gravitational collapse, causing the star's outer layers to explode in a supernova. Composed almost completely of neutrons, they are the densest-known stars in the universe, with densities comparable to the average density of an atomic nucleus. A neutron star in a faraway galaxy has a mass equal to 2.4 solar masses (1 solar mass = $M_{\odot}$ = mass of the sun = 1.99×10^{30} kg) and a diameter of 26 km.

a. What is the density ρ of this neutron star?
b. How does this neutron star's density compare to the density of a uranium nucleus, which has a diameter of about 15 fm (1 fm = 10^{-15} m)?

Solution

We can treat both the neutron star and the U-235 nucleus as spheres. Then the density for both is given by:

$$\rho = \frac{m}{V}$$

with

$$V = \frac{4}{3}\pi r^3$$

(a) The radius of the neutron star is $\frac{1}{2} \times 26\ \mathrm{km} = \frac{1}{2} \times 2.6 \times 10^4\ \mathrm{m} = 1.3 \times 10^4\ \mathrm{m}$ so the density of the neutron star is:

$$\begin{aligned}\rho &= \frac{m}{V}\\ &= \frac{m}{\frac{4}{3}\pi r^3}\\ &= \frac{2.4(1.99\times 10^{30}\ kg)}{\frac{4}{3}\pi(1.3\times 10^{4} m)^3}\\ &= 5.2\times 10^{17}\ kg/m^3\end{aligned}$$

(b) The radius of the U-235 nucleus is $\frac{1}{2}\times 15\times 10^{-15}\ \text{m} = 7.5\times 10^{-15}\ \text{m}$, so the density of the U-235 nucleus is:

$$\begin{aligned}\rho &= \frac{m}{V}\\ &= \frac{m}{\frac{4}{3}\pi r^3}\\ &= \frac{235\ amu\left(\frac{1.66\times 10^{-27}\ kg}{1\ amu}\right)}{\frac{4}{3}\pi(7.5\times 10^{-15} m)^3}\\ &= 2.2\times 10^{17}\ kg/m^3\end{aligned}$$

These values are fairly similar (same order of magnitude), but the nucleus is more than twice as dense as the neutron star.

? Exercise 10.3.1

Find the density of a neutron star with a mass of 1.97 solar masses and a diameter of 13 km, and compare it to the density of a hydrogen nucleus, which has a diameter of 1.75 fm (1 fm $= 1\times 10^{-15}$ m).

Answer

The density of the neutron star is $3.4\times 10^{18}\ \text{kg/m}^3$. The density of a hydrogen nucleus is $6.0\times 10^{17}\ \text{kg/m}^3$. The neutron star is 5.7 times denser than the hydrogen nucleus.

To hold positively charged protons together in the very small volume of a nucleus requires very strong attractive forces because the positively charged protons repel one another strongly at such short distances. The force of attraction that holds the nucleus together is the strong nuclear force. (The strong force is one of the four fundamental forces that are known to exist. The others are the electromagnetic force, the gravitational force, and the nuclear weak force.) This force acts between protons, between neutrons, and between protons and neutrons. It is very different from the electrostatic force that holds negatively charged electrons around a positively charged nucleus (the attraction between opposite charges). Over distances less than 10^{-15} meters and within the nucleus, the strong nuclear force is much stronger than electrostatic repulsions between protons; over larger distances and outside the nucleus, it is essentially nonexistent.

10.3.1: Nuclear Binding Energy

As a simple example of the energy associated with the strong nuclear force, consider the helium atom composed of two protons, two neutrons, and two electrons. The total mass of these six subatomic particles may be calculated as:

$$\underset{\text{protons}}{(2\times 1.0073\ \text{amu})} + \underset{\text{neutrons}}{(2\times 1.0087\ \text{amu})} + \underset{\text{electrons}}{(2\times 0.00055\ \text{amu})} = 4.0331\ \text{amu} \tag{10.3.2}$$

However, mass spectrometric measurements reveal that the mass of an ${}^{4}_{2}\text{He}$ atom is 4.0026 amu, less than the combined masses of its six constituent subatomic particles. This difference between the calculated and experimentally measured masses is known as the mass defect of the atom. In the case of helium, the mass defect indicates a “loss” in mass of 4.0331 amu – 4.0026 amu = 0.0305 amu. The loss in mass accompanying the formation of an atom from protons, neutrons, and electrons is due to the conversion of that mass into energy that is evolved as the atom forms. The nuclear binding energy is the energy produced when the atoms' nucleons are bound together; this is also the energy needed to break a nucleus into its constituent protons and neutrons. In comparison to chemical bond energies, nuclear binding energies are *vastly* greater, as we will learn in this section. Consequently, the energy changes associated with nuclear reactions are vastly greater than are those for chemical reactions.

The conversion between mass and energy is most identifiably represented by the mass-energy equivalence equation as stated by Albert Einstein:

$$E = mc^2 \tag{10.3.3}$$

where E is energy, m is mass of the matter being converted, and c is the speed of light in a vacuum. This equation can be used to find the amount of energy that results when matter is converted into energy. Using this mass-energy equivalence equation, the nuclear binding energy of a nucleus may be calculated from its **mass defect**, as demonstrated in Example $10.3.2$. A variety of units are commonly used for nuclear binding energies, including electron volts (eV), with 1 eV equaling the amount of energy necessary to the move the charge of an electron across an electric potential difference of 1 volt, making $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$.

✓ Example 10.3.2: Calculation of Nuclear Binding Energy

Determine the binding energy for the nuclide ${}^{4}_{2}\text{He}$ in:

a. joules per mole of nuclei
b. joules per nucleus
c. MeV per nucleus

Solution

The mass defect for a ${}^{4}_{2}\text{He}$ nucleus is 0.0305 amu, as shown previously. Determine the binding energy in joules per nuclide using the mass-energy equivalence equation. To accommodate the requested energy units, the mass defect must be expressed in kilograms (recall that 1 J = 1 kg m^2/s^2).

(a) First, express the mass defect in g/mol. This is easily done considering the *numerical equivalence* of atomic mass (amu) and molar mass (g/mol) that results from the definitions of the amu and mole units (refer to the previous discussion in the chapter on atoms, molecules, and ions if needed). The mass defect is therefore 0.0305 g/mol. To accommodate the units of the other terms in the mass-energy equation, the mass must be expressed in kg, since 1 J = 1 kg m^2/s^2. Converting grams into kilograms yields a mass defect of $3.05 \times 10^{-5} \text{ kg/mol}$. Substituting this quantity into the mass-energy equivalence equation yields:

$$E = mc^2 \qquad = \frac{3.05 \times 10^{-5}\ kg}{mol} \times \left(\frac{2.998 \times 10^{8}\ m}{s}\right)^2 = 2.74 \times 10^{12}\ kg\, m^2 s^{-2} mol^{-1} \qquad = 2.74 \times 10^{12}\ J/mol$$

Note that this tremendous amount of energy is associated with the conversion of a very small amount of matter (about 30 mg, roughly the mass of typical drop of water).

(b) The binding energy for a single nucleus is computed from the molar binding energy using Avogadro's number:

$$\begin{aligned} E &= 2.74 \times 10^{12}\ J\, mol^{-1} \times \frac{1\ mol}{6.022 \times 10^{23}\ nuclei} \\ &= 4.55 \times 10^{-12}\ J = 4.55\ pJ \end{aligned}$$

(c) Recall that $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$. Using the binding energy computed in part (b):

$$\begin{aligned} E &= 4.55 \times 10^{-12}\ J \times \frac{1\ eV}{1.602 \times 10^{-19}\ J} \\ &= 2.84 \times 10^{7}\ eV = 28.4\ MeV \end{aligned}$$

? Exercise 10.3.2

What is the binding energy for the nuclide $^{19}_{9}F$ (atomic mass: 18.9984 amu) in MeV per nucleus?

Answer

148.4 MeV

Because the energy changes for breaking and forming bonds are so small compared to the energy changes for breaking or forming nuclei, the changes in mass during all ordinary chemical reactions are virtually undetectable. As described in the chapter on thermochemistry, the most energetic chemical reactions exhibit enthalpies on the order of *thousands* of kJ/mol, which is equivalent to mass differences in the nanogram range (10^{-9} g). On the other hand, nuclear binding energies are typically on the order of *billions* of kJ/mol, corresponding to mass differences in the milligram range (10^{-3} g).

10.3.2: Nuclear Stability

A nucleus is stable if it cannot be transformed into another configuration without adding energy from the outside. Of the thousands of nuclides that exist, about 250 are stable. A plot of the number of neutrons versus the number of protons for stable nuclei reveals that the stable isotopes fall into a narrow band. This region is known as the band of stability (also called the belt, zone, or valley of stability). The straight line in Figure 10.3.1 represents nuclei that have a 1:1 ratio of protons to neutrons (n:p ratio). Note that the lighter stable nuclei, in general, have equal numbers of protons and neutrons. For example, nitrogen-14 has seven protons and seven neutrons. Heavier stable nuclei, however, have increasingly more neutrons than protons. For example: iron-56 has 30 neutrons and 26 protons, an n:p ratio of 1.15, whereas the stable nuclide lead-207 has 125 neutrons and 82 protons, an n:p ratio equal to 1.52. This is because larger nuclei have more proton-proton repulsions, and require larger numbers of neutrons to provide compensating strong forces to overcome these electrostatic repulsions and hold the nucleus together.

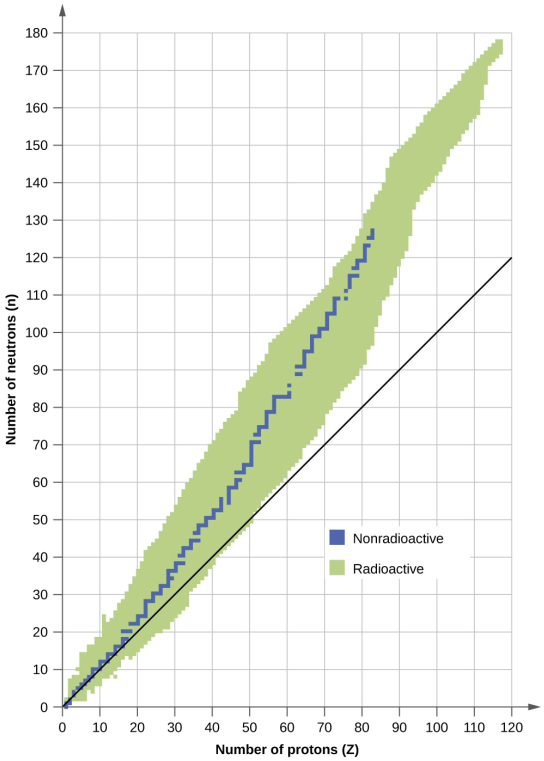


Figure 10.3.1: This plot shows the nuclides that are known to exist and those that are stable. The stable nuclides are indicated in blue, and the unstable nuclides are indicated in green. Note that all isotopes of elements with atomic numbers greater than 83 are unstable. The solid line is the line where n = Z.

The nuclei that are to the left or to the right of the band of stability are unstable and exhibit radioactivity. They change spontaneously (decay) into other nuclei that are either in, or closer to, the band of stability. These nuclear decay reactions convert one unstable isotope (or radioisotope) into another, more stable, isotope. We will discuss the nature and products of this radioactive decay in subsequent sections of this chapter.

Several observations may be made regarding the relationship between the stability of a nucleus and its structure. Nuclei with even numbers of protons, neutrons, or both are more likely to be stable (Table 10.3.1). Nuclei with certain numbers of nucleons, known as **magic numbers**, are stable against nuclear decay. These numbers of protons or neutrons (2, 8, 20, 28, 50, 82, and 126) make complete shells in the nucleus. These are similar in concept to the stable electron shells observed for the noble gases. Nuclei that have magic numbers of both protons and neutrons, such as $^{4}_{2}\text{He}$, $^{16}_{8}\text{O}$, $^{40}_{20}\text{Ca}$, and $^{208}_{82}\text{Pb}$ and are particularly stable. These trends in nuclear stability may be rationalized by considering a quantum mechanical model of nuclear energy states analogous to that used to describe electronic states earlier in this textbook. The details of this model are beyond the scope of this chapter.

Table 10.3.1: Stable Nuclear Isotopes

Number of Stable Isotopes	Proton Number	Neutron Number
157	even	even
53	even	odd
50	odd	even
5	odd	odd

The relative stability of a nucleus is correlated with its binding energy per nucleon, the total binding energy for the nucleus divided by the number or nucleons in the nucleus. For instance, the binding energy for a $^{4}_{2}\text{He}$ nucleus is therefore:

$$\frac{28.4\text{ MeV}}{4\text{ nucleons}} = 7.10\text{ MeV/nucleon} \tag{10.3.4}$$

The binding energy per nucleon of a nuclide on the curve shown in Figure 10.3.2

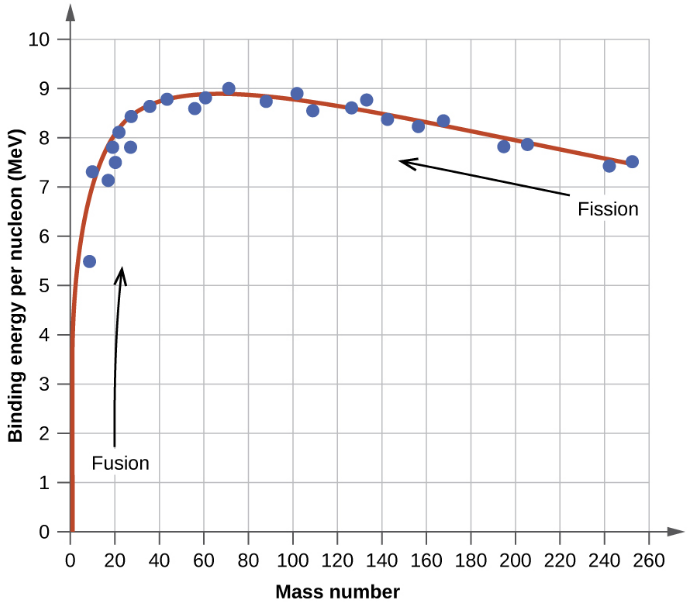


Figure 10.3.2: The binding energy per nucleon is largest for nuclides with mass number of approximately 56.

Example 10.3.3: Calculation of Binding Energy per Nucleon

The iron nuclide $^{56}_{26}\text{Fe}$ lies near the top of the binding energy curve (Figure 10.3.2) and is one of the most stable nuclides. What is the binding energy per nucleon (in MeV) for the nuclide $^{56}_{26}\text{Fe}$ (atomic mass of 55.9349 amu)?

Solution

As in Example, we first determine the mass defect of the nuclide, which is the difference between the mass of 26 protons, 30 neutrons, and 26 electrons, and the observed mass of an $^{56}_{26}\text{Fe}$ atom:

$$\begin{aligned}\text{Mass defect} &= [(26\times 1.0073\text{ amu})+(30\times 1.0087\text{ amu})+(26\times 0.00055\text{ amu})]-55.9349\text{ amu}\\ &=56.4651\text{ amu}-55.9349\text{ amu}\\ &=0.5302\text{ amu}\end{aligned}$$

We next calculate the binding energy for one nucleus from the mass defect using the mass-energy equivalence equation:

$$\begin{aligned}E &= mc^2 = 0.5302\text{ amu}\times\frac{1.6605\times 10^{-27}\text{ kg}}{1\text{ amu}}\times(2.998\times 10^{8}\text{ m/s})^2\\ &=7.913\times 10^{-11}\text{ kg}{\cdot}\text{m/s}^2\\ &=7.913\times 10^{-11}\text{ J}\end{aligned}$$

We then convert the binding energy in joules per nucleus into units of MeV per nuclide:

$$7.913\times 10^{-11}\text{ J}\times\frac{1\text{ MeV}}{1.602\times 10^{-13}\text{ J}}=493.9\text{ MeV}$$

Finally, we determine the binding energy per nucleon by dividing the total nuclear binding energy by the number of nucleons in the atom:

$$\text{Binding energy per nucleon}=\frac{493.9\text{ MeV}}{56}=8.820\text{ MeV/nucleon}$$

Note that this is almost 25% larger than the binding energy per nucleon for $^{4}_{2}\text{He}$.(Note also that this is the same process as in Example \(\PageIndex{2}\, but with the additional step of dividing the total nuclear binding energy by the number of nucleons.)

? Exercise 10.3.3

What is the binding energy per nucleon in $^{19}_{9}\text{F}$ (atomic mass, 18.9984 amu)?

Answer

7.810 MeV/nucleon

Summary

An atomic nucleus consists of protons and neutrons, collectively called nucleons. Although protons repel each other, the nucleus is held tightly together by a short-range, but very strong, force called the strong nuclear force. A nucleus has less mass than the total mass of its constituent nucleons. This “missing” mass is the mass defect, which has been converted into the binding energy that holds the nucleus together according to Einstein’s mass-energy equivalence equation, $E = mc^2$. Of the many nuclides that exist, only a small number are stable. Nuclides with even numbers of protons or neutrons, or those with magic numbers of nucleons, are especially likely to be stable. These stable nuclides occupy a narrow band of stability on a graph of number of protons versus number of neutrons. The binding energy per nucleon is largest for the elements with mass numbers near 56; these are the most stable nuclei.

10.3.3: Key Equations

- $E = mc^2$

Glossary

band of stability

(also, belt of stability, zone of stability, or valley of stability) region of graph of number of protons versus number of neutrons containing stable (nonradioactive) nuclides

binding energy per nucleon

total binding energy for the nucleus divided by the number of nucleons in the nucleus

electron volt (eV)

measurement unit of nuclear binding energies, with 1 eV equaling the amount energy due to the moving an electron across an electric potential difference of 1 volt

magic number

nuclei with specific numbers of nucleons that are within the band of stability

mass defect

difference between the mass of an atom and the summed mass of its constituent subatomic particles (or the mass “lost” when nucleons are brought together to form a nucleus)

mass-energy equivalence equation

Albert Einstein’s relationship showing that mass and energy are equivalent

nuclear binding energy

energy lost when an atom’s nucleons are bound together (or the energy needed to break a nucleus into its constituent protons and neutrons)

nuclear chemistry

study of the structure of atomic nuclei and processes that change nuclear structure

nucleon

collective term for protons and neutrons in a nucleus

nuclide

nucleus of a particular isotope

radioactivity

phenomenon exhibited by an unstable nucleon that spontaneously undergoes change into a nucleon that is more stable; an unstable nucleon is said to be radioactive

radioisotope

isotope that is unstable and undergoes conversion into a different, more stable isotope

strong nuclear force

force of attraction between nucleons that holds a nucleus together

- 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).

10.4: Transmutation and Nuclear Energy

Learning Objectives

- Describe the synthesis of transuranium nuclides
- Explain nuclear fission and fusion processes
- Relate the concepts of critical mass and nuclear chain reactions
- Summarize basic requirements for nuclear fission and fusion reactors

After the discovery of radioactivity, the field of nuclear chemistry was created and developed rapidly during the early twentieth century. A slew of new discoveries in the 1930s and 1940s, along with World War II, combined to usher in the Nuclear Age in the mid-twentieth century. Science learned how to create new substances, and certain isotopes of certain elements were found to possess the capacity to produce unprecedented amounts of energy, with the potential to cause tremendous damage during war, as well as produce enormous amounts of power for society's needs during peace.

10.4.1: Synthesis of Nuclides

Nuclear transmutation is the conversion of one nuclide into another. It can occur by the radioactive decay of a nucleus, or the reaction of a nucleus with another particle. The first manmade nucleus was produced in Ernest Rutherford's laboratory in 1919 by a transmutation reaction, the bombardment of one type of nuclei with other nuclei or with neutrons. Rutherford bombarded nitrogen atoms with high-speed α particles from a natural radioactive isotope of radium and observed protons resulting from the reaction:

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$$

The $^{17}_{8}\mathrm{O}$ and $^{1}_{1}\mathrm{H}$ nuclei that are produced are stable, so no further (nuclear) changes occur.

To reach the kinetic energies necessary to produce transmutation reactions, devices called particle accelerators are used. These devices use magnetic and electric fields to increase the speeds of nuclear particles. In all accelerators, the particles move in a vacuum to avoid collisions with gas molecules. When neutrons are required for transmutation reactions, they are usually obtained from radioactive decay reactions or from various nuclear reactions occurring in nuclear reactors. The Chemistry in Everyday Life feature that follows discusses a famous particle accelerator that made worldwide news.

CERN Particle Accelerator

Located near Geneva, the CERN ("Conseil Européen pour la Recherche Nucléaire," or European Council for Nuclear Research) Laboratory is the world's premier center for the investigations of the fundamental particles that make up matter. It contains the 27-kilometer (17 mile) long, circular Large Hadron Collider (LHC), the largest particle accelerator in the world (Figure 10.4.1). In the LHC, particles are boosted to high energies and are then made to collide with each other or with stationary targets at nearly the speed of light. Superconducting electromagnets are used to produce a strong magnetic field that guides the particles around the ring. Specialized, purpose-built detectors observe and record the results of these collisions, which are then analyzed by CERN scientists using powerful computers.

Figure 10.4.1: A small section of the LHC is shown with workers traveling along it. (credit: Christophe Delaere)

In 2012, CERN announced that experiments at the LHC showed the first observations of the Higgs boson, an elementary particle that helps explain the origin of mass in fundamental particles. This long-anticipated discovery made worldwide news and resulted in the awarding of the 2103 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

Prior to 1940, the heaviest-known element was uranium, whose atomic number is 92. Now, many artificial elements have been synthesized and isolated, including several on such a large scale that they have had a profound effect on society. One of these—element 93, neptunium (Np)—was first made in 1940 by McMillan and Abelson by bombarding uranium-238 with neutrons. The reaction creates unstable uranium-239, with a half-life of 23.5 minutes, which then decays into neptunium-239. Neptunium-239 is also radioactive, with a half-life of 2.36 days, and it decays into plutonium-239. The nuclear reactions are:

$$\begin{aligned} &^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U} \\ &^{239}_{92}\mathrm{U} \qquad \longrightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\mathrm{e} \quad t_{\frac{1}{2}} \quad \text{half-life} = 23.5\ \text{min} \\ &^{239}_{93}\mathrm{Np} \qquad \longrightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\mathrm{e} \quad t_{\frac{1}{2}} \quad \text{half-life} = 2.36\ \text{days} \end{aligned}$$

Plutonium is now mostly formed in nuclear reactors as a byproduct during the decay of uranium. Some of the neutrons that are released during U-235 decay combine with U-238 nuclei to form uranium-239; this undergoes β decay to form neptunium-239, which in turn undergoes β decay to form plutonium-239 as illustrated in the preceding three equations. It is possible to summarize these equations as:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U} \xrightarrow{\beta^-} {}^{239}_{93}\mathrm{Np} \xrightarrow{\beta^-} {}^{239}_{94}\mathrm{Pu}$$

Heavier isotopes of plutonium—Pu-240, Pu-241, and Pu-242—are also produced when lighter plutonium nuclei capture neutrons. Some of this highly radioactive plutonium is used to produce military weapons, and the rest presents a serious storage problem because they have half-lives from thousands to hundreds of thousands of years.

Although they have not been prepared in the same quantity as plutonium, many other synthetic nuclei have been produced. Nuclear medicine has developed from the ability to convert atoms of one type into other types of atoms. Radioactive isotopes of several dozen elements are currently used for medical applications. The radiation produced by their decay is used to image or treat various organs or portions of the body, among other uses.

The elements beyond element 92 (uranium) are called transuranium elements. As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval. Some of these elements are shown in Table 10.4.1.

Table 10.4.1: Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	$^{239}_{94}\mathrm{Pu} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{240}_{95}\mathrm{Am} + {}^{0}_{-1}\mathrm{e}$

Name	Symbol	Atomic Number	Reaction
curium	Cm	96	${}^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$
californium	Cf	98	${}^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{245}_{98}\mathrm{Cf} + {}^{1}_{0}\mathrm{n}$
einsteinium	Es	99	${}^{238}_{92}\mathrm{U} + 15\,{}^{1}_{0}\mathrm{n} \longrightarrow {}^{253}_{99}\mathrm{Es} + 7\,{}^{0}_{-1}\mathrm{e}$
mendelevium	Md	101	${}^{253}_{99}\mathrm{Es} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{256}_{101}\mathrm{Md} + {}^{1}_{0}\mathrm{n}$
nobelium	No	102	${}^{246}_{96}\mathrm{Cm} + {}^{12}_{6}\mathrm{C} \longrightarrow {}^{254}_{102}\mathrm{No} + 4\,{}^{1}_{0}\mathrm{n}$
rutherfordium	Rf	104	${}^{249}_{98}\mathrm{Cf} + {}^{12}_{6}\mathrm{C} \longrightarrow {}^{257}_{104}\mathrm{Rf} + 4\,{}^{1}_{0}\mathrm{n}$
seaborgium	Sg	106	${}^{206}_{82}\mathrm{Pb} + {}^{54}_{24}\mathrm{Cr} \longrightarrow {}^{257}_{106}\mathrm{Sg} + 3\,{}^{1}_{0}\mathrm{n}$ ${}^{249}_{98}\mathrm{Cf} + {}^{18}_{8}\mathrm{O} \longrightarrow {}^{263}_{106}\mathrm{Sg} + 4\,{}^{1}_{0}\mathrm{n}$
meitnerium	Mt	107	${}^{209}_{83}\mathrm{Bi} + {}^{58}_{26}\mathrm{Fe} \longrightarrow {}^{266}_{109}\mathrm{Mt} + {}^{1}_{0}\mathrm{n}$

10.4.2: Nuclear Fission

Many heavier elements with smaller binding energies per nucleon can decompose into more stable elements that have intermediate mass numbers and larger binding energies per nucleon—that is, mass numbers and binding energies per nucleon that are closer to the “peak” of the binding energy graph near 56. Sometimes neutrons are also produced. This decomposition is called fission, the breaking of a large nucleus into smaller pieces. The breaking is rather random with the formation of a large number of different products. Fission usually does not occur naturally, but is induced by bombardment with neutrons. The first reported nuclear fission occurred in 1939 when three German scientists, Lise Meitner, Otto Hahn, and Fritz Strassman, bombarded uranium-235 atoms with slow-moving neutrons that split the U-238 nuclei into smaller fragments that consisted of several neutrons and elements near the middle of the periodic table. Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure 10.4.2

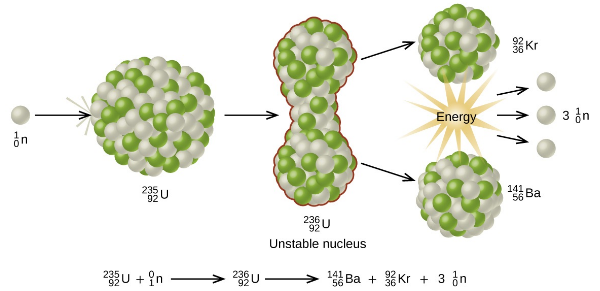
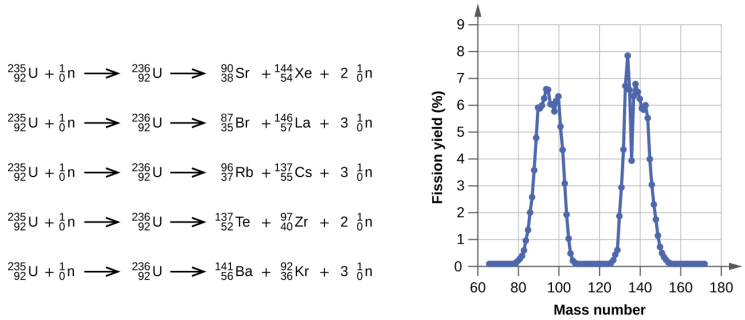


Figure 10.4.2: When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

A diagram is shown which has a white sphere labeled “superscript, 1, subscript 0, n” followed by a right-facing arrow and a large sphere composed of many smaller white and green spheres labeled “superscript, 235, subscript 92, U.” The single sphere has impacted the larger sphere. A right-facing arrow leads from the larger sphere to a vertical dumbbell shaped collection of the same white and green spheres labeled “superscript, 236, subscript 92, U, Unstable nucleus.” Two right-facing arrows lead from the top and bottom of this structure to two new spheres that are also composed of green and white spheres and are slightly smaller than the others. The top sphere is labeled “superscript, 92, subscript 36, K r” while the lower one is labeled “superscript, 141, subscript 56, B a.” A starburst pattern labeled “Energy” lies between these two spheres and has three right-facing arrows leading from it to three white spheres labeled “3, superscript, 1, subscript 0, n.” A balanced nuclear equation is written below the diagram and says “superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 236, subscript 92, U, yield arrow, superscript, 141, subscript 56, B a, plus sign, superscript, 92, subscript 36, K r, plus sign, 3, superscript, 1, subscript 0, n.”

Among the products of Meitner, Hahn, and Strassman’s fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances. A few of the many reactions that occur for U-235, and a graph showing the distribution of its fission products and their yields, are shown in Figure 10.4.3. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.



(a) (b)

Figure 10.4.3: (a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

Five nuclear equations and a graph are shown. The first equation is “superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 236, subscript 92, U, yield arrow, superscript, 90, subscript 38, S r, plus sign, superscript, 144, subscript 54, X e, plus sign, 2, superscript, 1, subscript 0, n.” The second equation is “superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 236, subscript 92, U, yield arrow, superscript, 87, subscript 35, B r, plus sign, superscript, 146, subscript 57, L a, plus sign, 3, superscript, 1, subscript 0, n.” The third equation is “superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 236, subscript 92, U, yield arrow, superscript, 97, subscript 37, R b, plus sign, superscript, 137, subscript 55, C s, plus sign, 3, superscript, 1, subscript 0, n.” The fourth equation is “superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 236, subscript 92, U, yield arrow, superscript, 137, subscript 52, T e, plus sign, superscript, 97, subscript 40, Z r, plus sign, 2, superscript, 1, subscript 0, n.” The fifth equation is “superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 236, subscript 92, U, yield arrow, superscript, 141, subscript 56, B a, plus sign, superscript, 92, subscript 36, K r, plus sign, 3, superscript, 1, subscript 0, n.” A graph is also shown where the y-axis is labeled “Fission yield, open parenthesis, percent sign, close parenthesis” and has values of 0 to 9 in increments of 1 while the x-axis is labeled “Mass number” and has values of 60 to 180 in increments of 20. The graph begins near point “65, 0” and rises rapidly to near “92, 6.6,” then drops just as rapidly to “107, 0” and remains there to point “127, 0.” The graph then rises again to near “132, 8,” then goes up and down a bit before falling to a point “153, 0,” and going horizontal.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this “lost” mass is converted into a very large amount of energy, about 1.8×10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

As described earlier, when undergoing fission U-235 produces two “medium-sized” nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear chain reaction (Figure 10.4.4). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

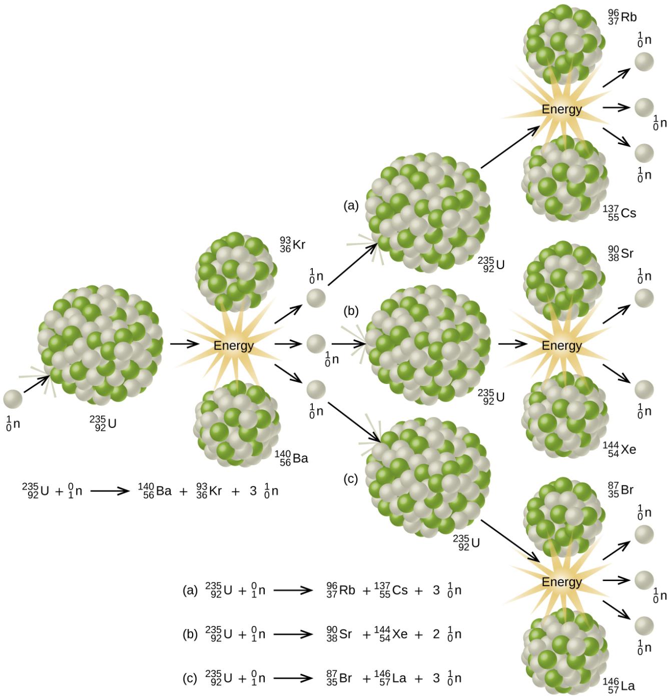


Figure 10.4.4: The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

A diagram is shown which has a white sphere labeled “superscript, 1, subscript 0, n” followed by a right-facing arrow and a large sphere composed of many smaller white and green spheres labeled “superscript, 235, subscript 92, U.” The single sphere has impacted the larger sphere. A right-facing arrow leads from the larger sphere to a pair of smaller spheres which are collections of the same white and green spheres. The upper of these two images is labeled “superscript, 93, subscript 36, K r” while the lower of the two is labeled “superscript, 142, subscript 56, B a.” A starburst pattern labeled “Energy” lies between these two spheres and has three right-facing arrows leading from it to three white spheres labeled “ superscript, 1, subscript 0, n.” An equation below this portion of the diagram reads ““superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 140, subscript 56, B a, plus sign, superscript 90, subscript 36, K r, plus sign, 3, superscript 1, subscript 0, n.” A right-facing arrow leads from each of these white spheres to three larger spheres, each composed of many smaller green and white spheres and labeled, from top to bottom as “a, superscript,235, subscript 92, U,” “b, superscript,235, subscript 92, U” and “c, superscript,235, subscript 92, U.” Each of these spheres is followed by a right-facing arrow which points to a pair of smaller spheres composed of the same green and white spheres with starburst patterns in between each pair labeled “Energy.” The spheres of the top pair are labeled, from top to bottom, “superscript, 96, subscript 37, R b” and “superscript, 137, subscript 55, C s.” The spheres of the middle pair are labeled, from top to bottom, “superscript, 90, subscript 38, S r” and “superscript, 144, subscript 54, X e.” The spheres of the bottom pair are labeled, from top to bottom, “superscript, 87, subscript 35, B r” and “superscript, 146, subscript 57, L a.” Each pair of spheres is followed by three right-facing arrows leading to three white spheres labeled “superscript, 1, subscript 0, n.” Below the diagram are three nuclear equations. Equation a reads “superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 96, subscript 37, R b, plus sign, superscript 137, subscript 55, C s, plus sign, 3, superscript 1, subscript 0, n.” Equation b reads “superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 90, subscript 38, S r, plus sign, superscript144, subscript 54, X e, plus sign, 2, superscript 1, subscript 0, n.” Equation c reads “superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 87, subscript 35, B r, plus sign, superscript 146, subscript 57, L a, plus sign, 3, superscript 1, subscript 0, n”

Material that can sustain a nuclear fission chain reaction is said to be fissile or fissionable. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a critical mass. An amount of fissionable material that cannot sustain a chain reaction is a subcritical mass. An amount of material in which there is an increasing rate of fission is known as a supercritical mass. The critical mass depends on the type of material: its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled (Figure 10.4.5).

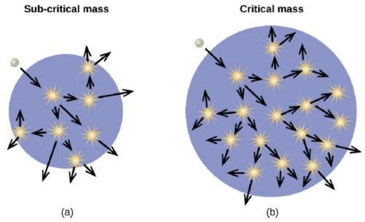


Figure 10.4.5: (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

The images are shown and labeled “a,” “b” and “c.” Image a, labeled “Sub-critical mass,” shows a blue circle background with a white sphere near the outer, top, left edge of the circle. A downward, right-facing arrow indicates that the white sphere enters the circle. Seven small, yellow starbursts are drawn in the blue circle and each has an arrow facing from it to outside the circle, in seemingly random directions. Image b, labeled “Critical mass,” shows a blue circle background with a white sphere near the outer, top, left edge of the circle. A downward, right-facing arrow indicates that the white sphere enters the circle. Seventeen small, yellow starbursts are drawn in the blue circle and each has an arrow facing from it to outside the circle, in seemingly random directions. Image c, labeled “Critical mass from neutron deflection,” shows a blue circle background, lying in a larger purple circle, with a white sphere near the outer, top, left edge of the purple circle. A downward, right-facing arrow indicates that the white sphere enters both of the circles. Thirteen small, yellow starbursts are drawn in the blue circle and each has an arrow facing from it to outside the blue circle, and a couple outside of the purple circle, in seemingly random directions.

An atomic bomb (Figure 10.4.6) contains several pounds of fissionable material, $^{235}_{92}\mathrm{U}$ or $^{239}_{94}\mathrm{Pu}$, a source of neutrons, and an explosive device for compressing it quickly into a small volume. When fissionable material is in small pieces, the proportion of neutrons that escape through the relatively large surface area is great, and a chain reaction does not take place. When the small pieces of fissionable material are brought together quickly to form a body with a mass larger than the critical mass, the relative number of escaping neutrons decreases, and a chain reaction and explosion result.

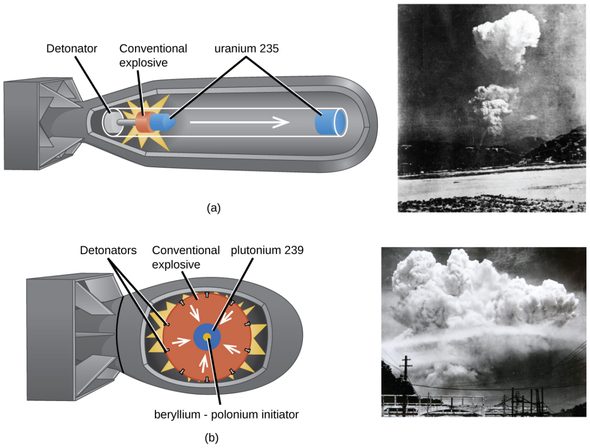


Figure 10.4.6: (a) The nuclear fission bomb that destroyed Hiroshima on August 6, 1945, consisted of two subcritical masses of U-235, where conventional explosives were used to fire one of the subcritical masses into the other, creating the critical mass for the nuclear explosion. (b) The plutonium bomb that destroyed Nagasaki on August 12, 1945, consisted of a hollow sphere of plutonium that was rapidly compressed by conventional explosives. This led to a concentration of plutonium in the center that was greater than the critical mass necessary for the nuclear explosion.

Two diagrams are shown, each to the left of a photo, and labeled “a” and “b.” Diagram a shows the outer casing of a bomb that has a long, tubular shape with a squared-off tail. Components in the shell show a tube with a white disk labeled “Detonator” on the left, an orange disk with a bright yellow starburst drawn around it labeled “Conventional explosive” in the middle and a right-facing arrow leading to a blue disk in the nose of the bomb labeled “uranium 235.” A small blue cone next to the orange disk is shares the label of “uranium 235.” A black and white photo next to this diagram shows a far-off shot of a rising cloud over a landscape. Diagram b shows the outer casing of a bomb that has a short, rounded shape with a squared-off tail. Components in the shell show a large orange circle labeled “Conventional explosive” with a series of black dots around its edge, labeled “Detonators,” and a yellow starburst behind it. White arrows face from the outer edge of the orange circle to a blue circle in the center with a yellow core. The blue circle is labeled “plutonium 239” while the yellow core is labeled “beryllium, dash, polonium initiator.” A black and white photo next to this diagram shows a far-off shot of a giant rising cloud over a landscape.

10.4.2.1: Fission Reactors

Chain reactions of fissionable materials can be controlled and sustained without an explosion in a nuclear reactor (Figure 10.4.7). Any nuclear reactor that produces power via the fission of uranium or plutonium by bombardment with neutrons must have at least five components: nuclear fuel consisting of fissionable material, a nuclear moderator, reactor coolant, control rods, and a shield and containment system. We will discuss these components in greater detail later in the section. The reactor works by separating the fissionable nuclear material such that a critical mass cannot be formed, controlling both the flux and absorption of neutrons to allow shutting down the fission reactions. In a nuclear reactor used for the production of electricity, the energy released by fission reactions is trapped as thermal energy and used to boil water and produce steam. The steam is used to turn a turbine, which powers a generator for the production of electricity.

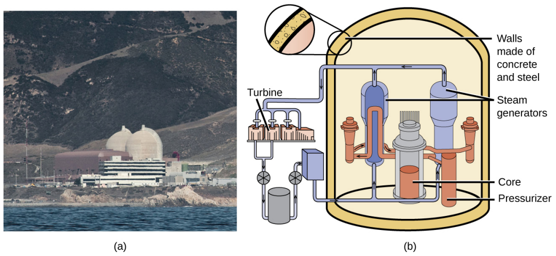


Figure 10.4.7: (a) The Diablo Canyon Nuclear Power Plant near San Luis Obispo is the only nuclear power plant currently in operation in California. The domes are the containment structures for the nuclear reactors, and the brown building houses the turbine where electricity is generated. Ocean water is used for cooling. (b) The Diablo Canyon uses a pressurized water reactor, one of a few different fission reactor designs in use around the world, to produce electricity. Energy from the nuclear fission reactions in the core heats water in a closed, pressurized system. Heat from this system produces steam that drives a turbine, which in turn produces electricity. (credit a: modification of work by “Mike” Michael L. Baird; credit b: modification of work by the Nuclear Regulatory Commission)

A photo labeled “a” and a diagram labeled “b” is shown. The photo is of a power plant with two large white domes and many buildings. The diagram shows a cylindrical container with thick walls labeled “Walls made of concrete and steel” and three main components inside. The first of these components is a pair of tall cylinders labeled “Steam generators” that sit to either side of a shorter cylinder labeled “Core.” Next to the core is a thin cylinder labeled “Pressurizer.” To the left of the outer walls is a set of pistons labeled “Turbines” that sit above a series of other equipment.

10.4.2.2: Nuclear Fuels

Nuclear fuel consists of a fissionable isotope, such as uranium-235, which must be present in sufficient quantity to provide a self-sustaining chain reaction. In the United States, uranium ores contain from 0.05–0.3% of the uranium oxide U_3O_8; the uranium in the ore is about 99.3% nonfissionable U-238 with only 0.7% fissionable U-235. Nuclear reactors require a fuel with a higher concentration of U-235 than is found in nature; it is normally enriched to have about 5% of uranium mass as U-235. At this concentration, it is not possible to achieve the supercritical mass necessary for a nuclear explosion. Uranium can be enriched by gaseous diffusion (the only method currently used in the US), using a gas centrifuge, or by laser separation.

In the gaseous diffusion enrichment plant where U-235 fuel is prepared, UF_6 (uranium hexafluoride) gas at low pressure moves through barriers that have holes just barely large enough for UF_6 to pass through. The slightly lighter $^{235}UF_6$ molecules diffuse through the barrier slightly faster than the heavier $^{238}UF_6$ molecules. This process is repeated through hundreds of barriers, gradually increasing the concentration of $^{235}UF_6$ to the level needed by the nuclear reactor. The basis for this process, Graham’s law, is described in the chapter on gases. The enriched UF_6 gas is collected, cooled until it solidifies, and then taken to a fabrication facility where it is made into fuel assemblies. Each fuel assembly consists of fuel rods that contain many thimble-sized, ceramic-encased, enriched uranium (usually UO_2) fuel pellets. Modern nuclear reactors may contain as many as 10 million fuel pellets. The amount of energy in each of these pellets is equal to that in almost a ton of coal or 150 gallons of oil.

10.4.2.3: Nuclear Moderators

Neutrons produced by nuclear reactions move too fast to cause fission (Figure 21.5.5). They must first be slowed to be absorbed by the fuel and produce additional nuclear reactions. A nuclear moderator is a substance that slows the neutrons to a speed that is low enough to cause fission. Early reactors used high-purity graphite as a moderator. Modern reactors in the US exclusively use heavy water $(^2_1H_2O)$ or light water (ordinary H_2O), whereas some reactors in other countries use other materials, such as carbon dioxide, beryllium, or graphite.

10.4.2.4: Reactor Coolants

A nuclear reactor coolant is used to carry the heat produced by the fission reaction to an external boiler and turbine, where it is transformed into electricity. Two overlapping coolant loops are often used; this counteracts the transfer of radioactivity from the reactor to the primary coolant loop. All nuclear power plants in the US use water as a coolant. Other coolants include molten sodium, lead, a lead-bismuth mixture, or molten salts.

10.4.2.5: Control Rods

Nuclear reactors use control rods (Figure 10.4.8) to control the fission rate of the nuclear fuel by adjusting the number of slow neutrons present to keep the rate of the chain reaction at a safe level. Control rods are made of boron, cadmium, hafnium, or other elements that are able to absorb neutrons. Boron-10, for example, absorbs neutrons by a reaction that produces lithium-7 and alpha particles:

$$^{10}_{5}\text{B} + ^{1}_{0}\text{n} \longrightarrow ^{7}_{3}\text{Li} + ^{4}_{2}\text{He}$$

When control rod assemblies are inserted into the fuel element in the reactor core, they absorb a larger fraction of the slow neutrons, thereby slowing the rate of the fission reaction and decreasing the power produced. Conversely, if the control rods are removed, fewer neutrons are absorbed, and the fission rate and energy production increase. In an emergency, the chain reaction can be shut down by fully inserting all of the control rods into the nuclear core between the fuel rods.

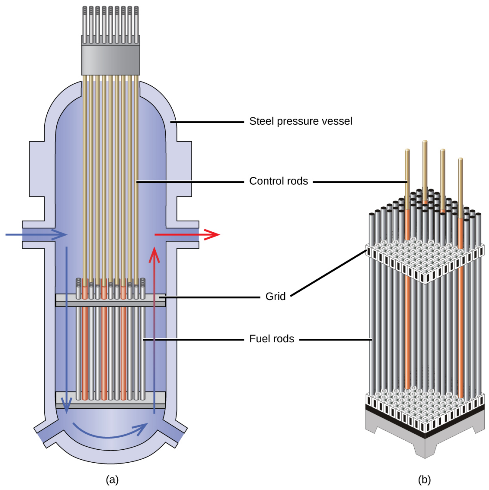


Figure 10.4.8: The nuclear reactor core shown in (a) contains the fuel and control rod assembly shown in (b). (credit: modification of work by E. Generalic, glossary.periodni.com/glossar...en=control+rod)

Two diagrams are shown and labeled “a” and “b.” Diagram a shows a cut-away view of a vertical tube with a flat, horizontal plate near the bottom that connects to a series of vertical pipes lined up next to one another and labeled “Fuel rods.” A second horizontal plate labeled “Grid” lies at the top of the pipes and a second set of thinner, vertical pipes, labeled “Control rods,” leads from this plate to the top of the container. The walls of the container are labeled “Steel pressure vessel.” A blue, right-facing arrow leads from an entry point in the left side of the container and is followed by a second, down-facing blue arrow and a curved, right-facing arrow that trace along the outer, bottom edge of the container. A blue and red arrow follows these and faces up the right side of the container to an exit near the right face where a red, right-facing arrow leads out. Diagram b is a cut-away image of a vertical, rectangular, three dimensional set of vertical pipes. The pipes are labeled “Fuel rods” and are inserted into an upper and lower horizontal plate labeled “Grid.” Four thin rods extend above the pipes and are labeled “Control rods.

10.4.2.6: Shield and Containment System

During its operation, a nuclear reactor produces neutrons and other radiation. Even when shut down, the decay products are radioactive. In addition, an operating reactor is thermally very hot, and high pressures result from the circulation of water or another coolant through it. Thus, a reactor must withstand high temperatures and pressures, and must protect operating personnel from the radiation. Reactors are equipped with a containment system (or shield) that consists of three parts:

1. The reactor vessel, a steel shell that is 3–20-centimeters thick and, with the moderator, absorbs much of the radiation produced by the reactor
2. A main shield of 1–3 meters of high-density concrete
3. A personnel shield of lighter materials that protects operators from γ rays and X-rays

In addition, reactors are often covered with a steel or concrete dome that is designed to contain any radioactive materials might be released by a reactor accident.

Video 10.4.1: Click here to watch a 3-minute video from the Nuclear Energy Institute on how nuclear reactors work.

Nuclear power plants are designed in such a way that they cannot form a supercritical mass of fissionable material and therefore cannot create a nuclear explosion. But as history has shown, failures of systems and safeguards can cause catastrophic accidents, including chemical explosions and nuclear meltdowns (damage to the reactor core from overheating). The following Chemistry in Everyday Life feature explores three infamous meltdown incidents.

Nuclear Accidents

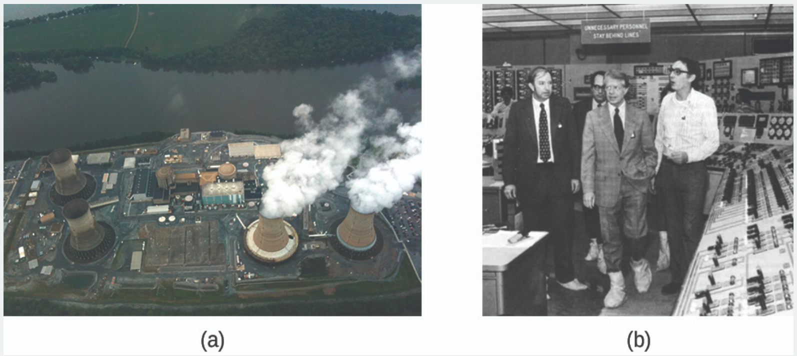
The importance of cooling and containment are amply illustrated by three major accidents that occurred with the nuclear reactors at nuclear power generating stations in the United States (Three Mile Island), the former Soviet Union (Chernobyl), and Japan (Fukushima).

In March 1979, the cooling system of the Unit 2 reactor at Three Mile Island Nuclear Generating Station in Pennsylvania failed, and the cooling water spilled from the reactor onto the floor of the containment building. After the pumps stopped, the reactors overheated due to the high radioactive decay heat produced in the first few days after the nuclear reactor shut down. The temperature of the core climbed to at least 2200 °C, and the upper portion of the core began to melt. In addition, the zirconium alloy cladding of the fuel rods began to react with steam and produced hydrogen:

$$\mathrm{Zr}(s) + 2\,\mathrm{H_2O}(g) \longrightarrow \mathrm{ZrO_2}(s) + 2\,\mathrm{H_2}(g)$$

The hydrogen accumulated in the confinement building, and it was feared that there was danger of an explosion of the mixture of hydrogen and air in the building. Consequently, hydrogen gas and radioactive gases (primarily krypton and xenon) were vented from the building. Within a week, cooling water circulation was restored and the core began to cool. The plant was closed for nearly 10 years during the cleanup process.

Although zero discharge of radioactive material is desirable, the discharge of radioactive krypton and xenon, such as occurred at the Three Mile Island plant, is among the most tolerable. These gases readily disperse in the atmosphere and thus do not produce highly radioactive areas. Moreover, they are noble gases and are not incorporated into plant and animal matter in the food chain. Effectively none of the heavy elements of the core of the reactor were released into the environment, and no cleanup of the area outside of the containment building was necessary (Figure 10.4.9).


(a)

(b)

Figure 10.4.9: (a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control room a few days after the accident in 1979.

Two photos, labeled "a" and "b" are shown. Photo a is an aerial view of a nuclear power plant. Photo b shows a small group of men walking through a room filled with electronics.

Another major nuclear accident involving a reactor occurred in April 1986, at the Chernobyl Nuclear Power Plant in Ukraine, which was still a part of the former Soviet Union. While operating at low power during an unauthorized experiment with some of its safety devices shut off, one of the reactors at the plant became unstable. Its chain reaction became uncontrollable and increased to a level far beyond what the reactor was designed for. The steam pressure in the reactor rose to between 100 and 500 times the full power pressure and ruptured the reactor. Because the reactor was not enclosed in a containment building, a large amount of radioactive material spewed out, and additional fission products were released, as the graphite (carbon) moderator of the core ignited and burned. The fire was controlled, but over 200 plant workers and firefighters developed acute radiation sickness and at least 32 soon died from the effects of the radiation. It is predicted that about 4000 more deaths will occur among emergency workers and former Chernobyl residents from radiation-induced cancer and leukemia. The reactor has since been encapsulated in steel and concrete, a now-decaying structure known as the sarcophagus. Almost 30 years later, significant radiation problems still persist in the area, and Chernobyl largely remains a wasteland.

In 2011, the Fukushima Daiichi Nuclear Power Plant in Japan was badly damaged by a 9.0-magnitude earthquake and resulting tsunami. Three reactors up and running at the time were shut down automatically, and emergency generators came online to power electronics and coolant systems. However, the tsunami quickly flooded the emergency generators and cut power to the pumps that circulated coolant water through the reactors. High-temperature steam in the reactors reacted with zirconium alloy to produce hydrogen gas. The gas escaped into the containment building, and the mixture of hydrogen and air exploded. Radioactive material was released from the containment vessels as the result of deliberate venting to reduce the hydrogen pressure, deliberate discharge of coolant water into the sea, and accidental or uncontrolled events.

An evacuation zone around the damaged plant extended over 12.4 miles away, and an estimated 200,000 people were evacuated from the area. All 48 of Japan's nuclear power plants were subsequently shut down, remaining shuttered as of December 2014. Since the disaster, public opinion has shifted from largely favoring to largely opposing increasing the use of nuclear power plants, and a restart of Japan's atomic energy program is still stalled (Figure 10.4.10).

(a)

(b)

Figure 10.4.10: (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by "Live Action Hero"/Flickr)

A photo and a map, labeled "a" and "b," respectively, are shown. Photo a shows a man in a body-covering safety suit working near a series of blue, plastic coated containers. Map b shows a section of land with the ocean on each side. Near the upper right side of the land is a small red dot, labeled "greater than, 12.5, m R backslash, h r," that is surrounded by a zone of orange that extends in the upper left direction labeled "2.17, dash, 12.5, m R backslash, h r." The orange is surrounded by an outline of yellow labeled "1.19, dash, 2.17, m R backslash, h r" and a wider outline of green labeled "0.25, dash, 1.19, m R backslash, h r." A large area of light blue, labeled "0.03, dash, 0.25, m R backslash, h r" surrounds the green area and extends to the lower middle of the map. A large section of the lower middle and left of the land is covered by dark blue, labeled "less than 0.03, m R backslash, h r."

The energy produced by a reactor fueled with enriched uranium results from the fission of uranium as well as from the fission of plutonium produced as the reactor operates. As discussed previously, the plutonium forms from the combination of neutrons and the uranium in the fuel. In any nuclear reactor, only about 0.1% of the mass of the fuel is converted into energy. The other 99.9% remains in the fuel rods as fission products and unused fuel. All of the fission products absorb neutrons, and after a period of several months to a few years, depending on the reactor, the fission products must be removed by changing the fuel rods. Otherwise, the concentration of these fission products would increase and absorb more neutrons until the reactor could no longer operate.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

10.4.3: Nuclear Fusion and Fusion Reactors

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:

$$4\,{}^{1}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + 2\,{}^{0}_{+1}$$

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, ${}^{2}_{1}$ and a triton, ${}^{3}_{1}$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$${}^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + 2\,{}^{1}_{0}\text{n}$$

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.

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.

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 10.4.11). 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.

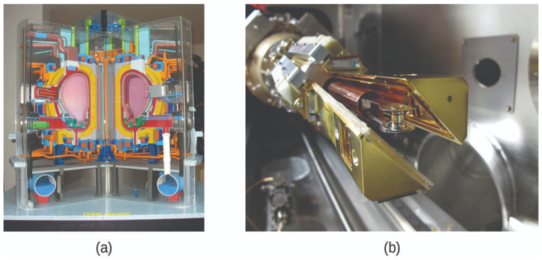

(a) (b)

Figure 10.4.11: (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 large-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)

Two photos are shown and labeled "a" and "b." Photo a shows a model of the ITER reactor made up of colorful components. Photo b shows a close-up view of the end of a long, mechanical arm made up of many metal components.

Summary

It is possible to produce new atoms by bombarding other atoms with nuclei or high-speed particles. The products of these transmutation reactions can be stable or radioactive. A number of artificial elements, including technetium, astatine, and the transuranium elements, have been produced in this way.

Nuclear power as well as nuclear weapon detonations can be generated through fission (reactions in which a heavy nucleus is split into two or more lighter nuclei and several neutrons). Because the neutrons may induce additional fission reactions when they combine with other heavy nuclei, a chain reaction can result. Useful power is obtained if the fission process is carried out in a nuclear reactor. The conversion of light nuclei into heavier nuclei (fusion) also produces energy. At present, this energy has not been contained adequately and is too expensive to be feasible for commercial energy production.

Glossary

chain reaction

repeated fission caused when the neutrons released in fission bombard other atoms

containment system

(also, shield) a three-part structure of materials that protects the exterior of a nuclear fission reactor and operating personnel from the high temperatures, pressures, and radiation levels inside the reactor

control rod

material inserted into the fuel assembly that absorbs neutrons and can be raised or lowered to adjust the rate of a fission reaction

critical mass

amount of fissionable material that will support a self-sustaining (nuclear fission) chain reaction

fissile (or fissionable)

when a material is capable of sustaining a nuclear fission reaction

fission

splitting of a heavier nucleus into two or more lighter nuclei, usually accompanied by the conversion of mass into large amounts of energy

fusion

combination of very light nuclei into heavier nuclei, accompanied by the conversion of mass into large amounts of energy

fusion reactor

nuclear reactor in which fusion reactions of light nuclei are controlled

nuclear fuel

fissionable isotope present in sufficient quantities to provide a self-sustaining chain reaction in a nuclear reactor

nuclear moderator

substance that slows neutrons to a speed low enough to cause fission

nuclear reactor
environment that produces energy via nuclear fission in which the chain reaction is controlled and sustained without explosion

nuclear transmutation
conversion of one nuclide into another nuclide

particle accelerator
device that uses electric and magnetic fields to increase the kinetic energy of nuclei used in transmutation reactions

reactor coolant
assembly used to carry the heat produced by fission in a reactor to an external boiler and turbine where it is transformed into electricity

subcritical mass
amount of fissionable material that cannot sustain a chain reaction; less than a critical mass

supercritical mass
amount of material in which there is an increasing rate of fission

transmutation reaction
bombardment of one type of nuclei with other nuclei or neutrons

transuranium element
element with an atomic number greater than 92; these elements do not occur in nature

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10.5: Uses of Radioisotopes

Learning Objectives

- List common applications of radioactive isotopes

Radioactive isotopes have the same chemical properties as stable isotopes of the same element, but they emit radiation, which can be detected. If we replace one (or more) atom(s) with radioisotope(s) in a compound, we can track them by monitoring their radioactive emissions. This type of compound is called a radioactive tracer (or radioactive label). Radioisotopes are used to follow the paths of biochemical reactions or to determine how a substance is distributed within an organism. Radioactive tracers are also used in many medical applications, including both diagnosis and treatment. They are used to measure engine wear, analyze the geological formation around oil wells, and much more.

Radioisotopes have revolutionized medical practice, where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States. Four typical examples of radioactive tracers used in medicine are technetium-99 $\left({}^{99}_{43}\mathrm{Tc}\right)$, thallium-201 $\left({}^{201}_{81}\mathrm{Tl}\right)$, iodine-131 $\left({}^{131}_{53}\mathrm{I}\right)$, and sodium-24 $\left({}^{24}_{11}\mathrm{Na}\right)$. Damaged tissues in the heart, liver, and lungs absorb certain compounds of technetium-99 preferentially. After it is injected, the location of the technetium compound, and hence the damaged tissue, can be determined by detecting the γ rays emitted by the Tc-99 isotope. Thallium-201 (Figure $10.5.1$) becomes concentrated in healthy heart tissue, so the two isotopes, Tc-99 and Tl-201, are used together to study heart tissue. Iodine-131 concentrates in the thyroid gland, the liver, and some parts of the brain. It can therefore be used to monitor goiter and treat thyroid conditions, such as Grave's disease, as well as liver and brain tumors. Salt solutions containing compounds of sodium-24 are injected into the bloodstream to help locate obstructions to the flow of blood.

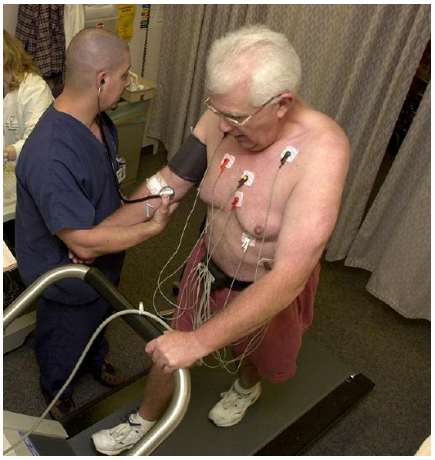

Figure 10.5.1: Administering thallium-201 to a patient and subsequently performing a stress test offer medical professionals an opportunity to visually analyze heart function and blood flow. (credit: modification of work by "Blue0ctane"/Wikimedia Commons)

A medical professional is assisting a topless elderly man on a treadmill with sensors and electrical wires connected to his torso.

Radioisotopes used in medicine typically have short half-lives—for example, the ubiquitous Tc-99m has a half-life of 6.01 hours. This makes Tc-99m essentially impossible to store and prohibitively expensive to transport, so it is made on-site instead. Hospitals and other medical facilities use Mo-99 (which is primarily extracted from U-235 fission products) to generate Tc-99. Mo-99 undergoes β decay with a half-life of 66 hours, and the Tc-99 is then chemically extracted (Figure $10.5.2$). The parent nuclide Mo-99 is part of a molybdate ion, $\mathrm{MoO_4^{2-}}$; when it decays, it forms the pertechnetate ion, $\mathrm{TcO_4^-}$. These two water-soluble ions are separated by column chromatography, with the higher charge molybdate ion adsorbing onto the alumina in the column, and the lower charge pertechnetate ion passing through the column in the solution. A few micrograms of Mo-99 can produce enough Tc-99 to perform as many as 10,000 tests.

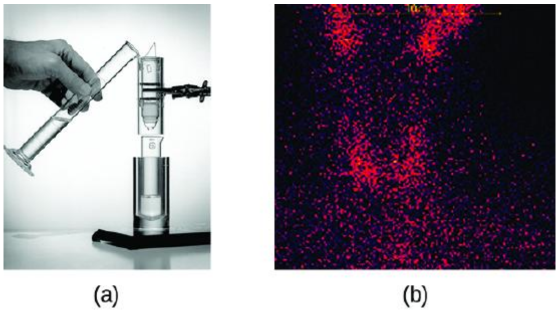

Figure 10.5.2: (a) The first Tc-99m generator (circa 1958) is used to separate Tc-99 from Mo-99. The $\mathrm{MoO_4^{2-}}$ *is retained by the matrix in the column, whereas the* $\mathrm{TcO_4^-}$ *passes through and is collected. (b) Tc-99 was used in this scan of the neck of a patient with Grave's disease. The scan shows the location of high concentrations of Tc-99. (credit a: modification of work by the Department of Energy; credit b: modification of work by "MBq"/Wikimedia Commons)*

The first image shows a hand pouring a liquid from a measuring cylinder into a column held up by a clamp. Below the column is a glass tube. The second picture shows red dots on a dark background dispersed everywhere with four spots of heavily concentrated regions.

Radioisotopes can also be used, typically in higher doses than as a tracer, as treatment. Radiation therapy is the use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing (Figure 10.5.3). A cancer patient may receive external beam radiation therapy delivered by a machine outside the body, or internal radiation therapy (brachytherapy) from a radioactive substance that has been introduced into the body. Note that chemotherapy is similar to internal radiation therapy in that the cancer treatment is injected into the body, but differs in that chemotherapy uses chemical rather than radioactive substances to kill the cancer cells.

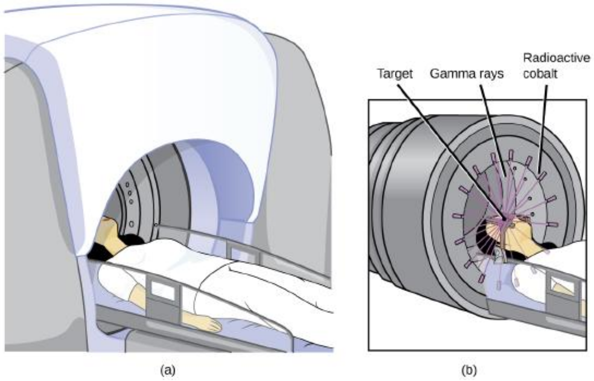

Figure 10.5.3: The cartoon in (a) shows a cobalt-60 machine used in the treatment of cancer. The diagram in (b) shows how the gantry of the Co-60 machine swings through an arc, focusing radiation on the targeted region (tumor) and minimizing the amount of radiation that passes through nearby regions.

A. A woman lies down as she goes into a dome shaped medical machine. B. A closer view of the women's head shows gamma rays from radioactive cobalt attacks the target on the woman's head.

Cobalt-60 is a synthetic radioisotope produced by the neutron activation of Co-59, which then undergoes β decay to form Ni-60, along with the emission of γ radiation. The overall process is:

$$\mathrm{^{59}_{27}Co} + \mathrm{^{1}_{0}n} \longrightarrow \mathrm{^{60}_{27}Co} \longrightarrow \mathrm{^{60}_{28}Ni} + {}^{0}_{-1}\beta + 2\,{}^{0}_{0}\gamma$$

The overall decay scheme for this is shown graphically in Figure 10.5.4

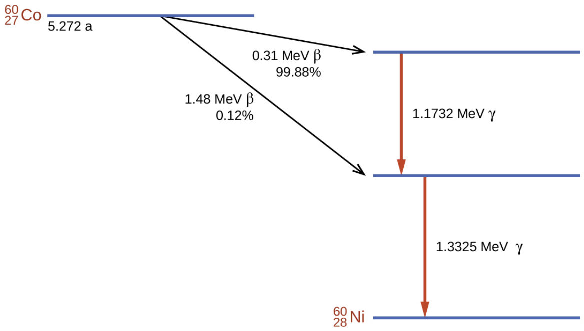

Figure 10.5.4: Co-60 undergoes a series of radioactive decays. The γ emissions are used for radiation therapy.

Radioisotopes are used in diverse ways to study the mechanisms of chemical reactions in plants and animals. These include labeling fertilizers in studies of nutrient uptake by plants and crop growth, investigations of digestive and milk-producing processes in cows, and studies on the growth and metabolism of animals and plants.

For example, the radioisotope C-14 was used to elucidate the details of how photosynthesis occurs. The overall reaction is:

$$6\,\mathrm{CO_2}(g) + 6\,\mathrm{H_2O}(l) \longrightarrow \mathrm{C_6H_{12}O_6}(s) + 6\,\mathrm{O_2}(g),$$

but the process is much more complex, proceeding through a series of steps in which various organic compounds are produced. In studies of the pathway of this reaction, plants were exposed to CO_2 containing a high concentration of $^{14}_{6}C$. At regular intervals, the plants were analyzed to determine which organic compounds contained carbon-14 and how much of each compound was present. From the time sequence in which the compounds appeared and the amount of each present at given time intervals, scientists learned more about the pathway of the reaction.

Commercial applications of radioactive materials are equally diverse (Figure 10.5.5). They include determining the thickness of films and thin metal sheets by exploiting the penetration power of various types of radiation. Flaws in metals used for structural purposes can be detected using high-energy gamma rays from cobalt-60 in a fashion similar to the way X-rays are used to examine the human body. In one form of pest control, flies are controlled by sterilizing male flies with γ radiation so that females breeding with them do not produce offspring. Many foods are preserved by radiation that kills microorganisms that cause the foods to spoil.

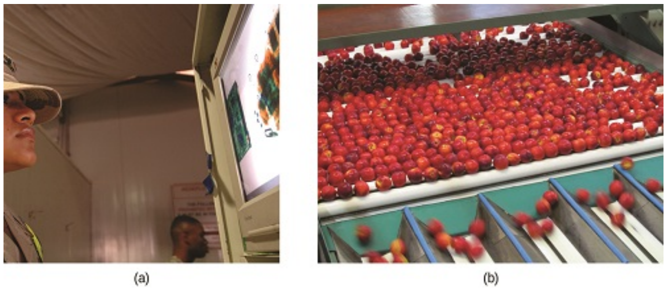
(a)
(b)

Figure 10.5.5: Common commercial uses of radiation include (a) X-ray examination of luggage at an airport and (b) preservation of food. (credit a: modification of work by the Department of the Navy; credit b: modification of work by the US Department of Agriculture)

A. A man is observing a monitor which shows the X-ray of luggages. B. Many apples on processing belts.

Americium-241, an α emitter with a half-life of 458 years, is used in tiny amounts in ionization-type smoke detectors (Figure 10.5.6). The α emissions from Am-241 ionize the air between two electrode plates in the ionizing chamber. A battery supplies a potential that causes movement of the ions, thus creating a small electric current. When smoke enters the chamber, the movement of the ions is impeded, reducing the conductivity of the air. This causes a marked drop in the current, triggering an alarm.

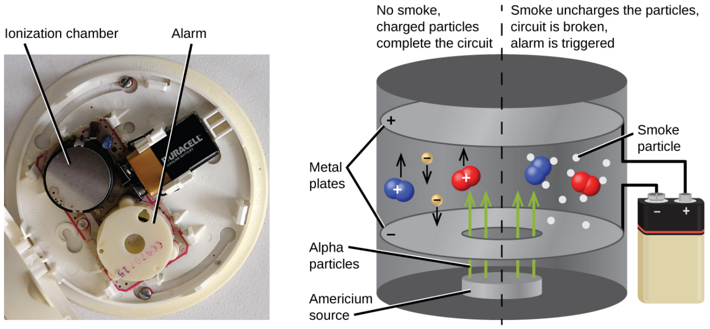

Figure 10.5.6: Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by “Muffet”/Wikimedia Commons)

The inside of a smoke detector is shown with the alarm and ionization chamber labeled. In the picture beside it, a schematic shows the mechanisms of a smoke detector. The two oppositely charged metals plates in the detector are shown along with the Americium source on the bottom part emitting alpha particles. The schematic is divided into two parts, one to show the presence and the other for the absence of smoke.

Summary

Compounds known as radioactive tracers can be used to follow reactions, track the distribution of a substance, diagnose and treat medical conditions, and much more. Other radioactive substances are helpful for controlling pests, visualizing structures, providing fire warnings, and for many other applications. Hundreds of millions of nuclear medicine tests and procedures, using a wide variety of radioisotopes with relatively short half-lives, are performed every year in the US. Most of these radioisotopes have relatively short half-lives; some are short enough that the radioisotope must be made on-site at medical facilities. Radiation therapy uses high-energy radiation to kill cancer cells by damaging their DNA. The radiation used for this treatment may be delivered externally or internally.

Glossary

chemotherapy

similar to internal radiation therapy, but chemical rather than radioactive substances are introduced into the body to kill cancer cells

external beam radiation therapy

radiation delivered by a machine outside the body

internal radiation therapy

(also, brachytherapy) radiation from a radioactive substance introduced into the body to kill cancer cells

radiation therapy

use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing

radioactive tracer

(also, radioactive label) radioisotope used to track or follow a substance by monitoring its radioactive emissions

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10.6: Biological Effects of Radiation

Learning Objectives

- Describe the biological impact of ionizing radiation.
- Define units for measuring radiation exposure.
- Explain the operation of common tools for detecting radioactivity.
- List common sources of radiation exposure in the US.

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure 10.6.1).

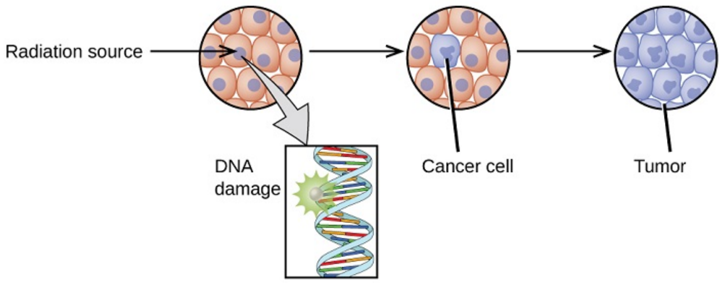

Figure 10.6.1: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

A diagram is shown which has a white sphere followed by a right-facing arrow and a large sphere composed of many smaller white and green spheres. The single sphere has impacted the larger sphere. A right-facing arrow leads from the larger sphere to a pair of smaller spheres which are collections of the same white and green spheres. A starburst pattern lies between these two spheres and has three right-facing arrows leading from it to two white spheres and a circle full of ten smaller, peach-colored circles with purple dots in their centers. An arrow leads downward from this circle to a box that contains a helical shape with a starburst near its top left side and is labeled "D N A damage." A right-facing arrow leads from this circle to a second circle, with nine smaller, peach-colored circles with purple dots in their centers and one fully purple small circle labeled "Cancer cell." A right-facing arrow leads to a final circle, this time full of the purple cells, that is labeled "Tumor."

10.6.1: Ionizing vs. Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure 10.6.2).

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Figure 10.6.2: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

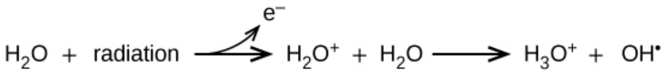

Figure 10.6.3.

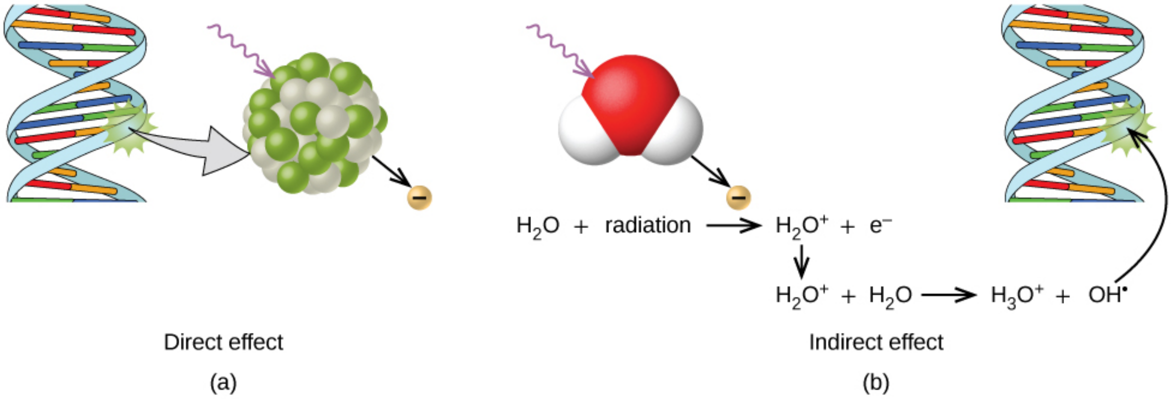

Figure 10.6.3: Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

10.6.2: Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material (Figure 10.6.4). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.

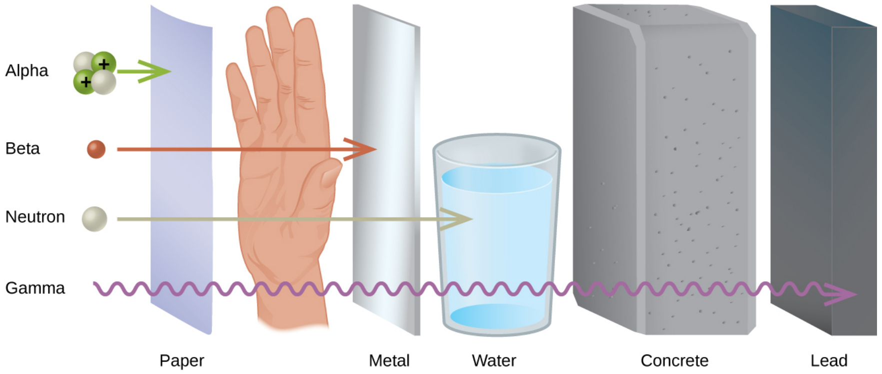

Figure 10.6.4: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.

A diagram shows four particles in a vertical column on the left, followed by an upright sheet of paper, a person's hand, an upright sheet of metal, a glass of water, a thick block of concrete and an upright, thick piece of lead. The top particle listed is made up of two white spheres and two green spheres that are labeled with positive signs and is labeled "Alpha." A right-facing arrow leads from this to the paper. The second particle is a red sphere labeled "Beta" and is followed by a right-facing arrow that passes through the paper and stops at the hand. The third particle is a white sphere labeled "Neutron" and is followed by a right-facing arrow that passes through the paper, hand and metal but is stopped at the glass of water. The fourth particle is shown by a squiggly arrow and it passes through all of the substances but stops at the lead. Terms at the bottom read, from left to right, "Paper," "Metal," "Water," "Concrete" and "Lead."

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238, which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above.

Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure 10.6.5).

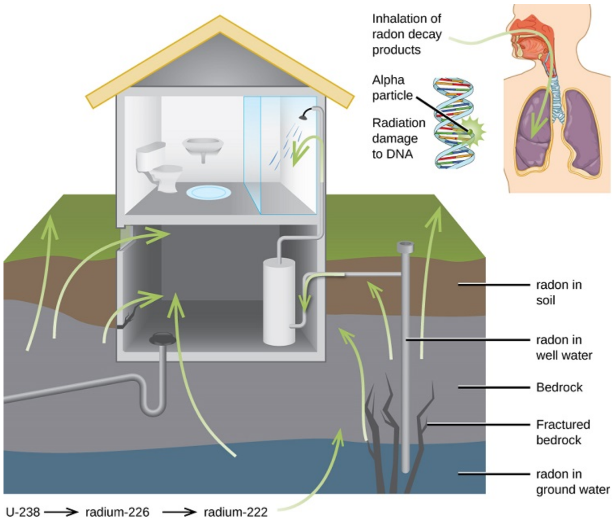

Figure 10.6.5: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

A cut-away image of the side of a house and four layers of the ground it rests on is shown, as well as a second cut-away image of a person's head and chest cavity. The house is shown with a restroom on the second floor and a basement with a water heater as the first floor. Green arrows lead from the lowest ground layer, labeled "radon in ground water," from the third ground layer, labeled "Bedrock" and "Fractured bedrock," from the second layer, labeled "radon in well water," and from the top layer, labeled "radon in soil to the inside of the basement area. In the smaller image of the torso, a green arrow is shown to enter the person's nasal passage and travel to the lungs. This is labeled "Inhalation of radon decay products." A small coiled, helical structure next to the torso is labeled "alpha particle" on one section where it has a starburst pattern and "Radiation damage to D N A" on another segment.

Radon is found in buildings across the country, with amounts dependent on location. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the level found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

10.6.3: Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure 10.6.6). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.

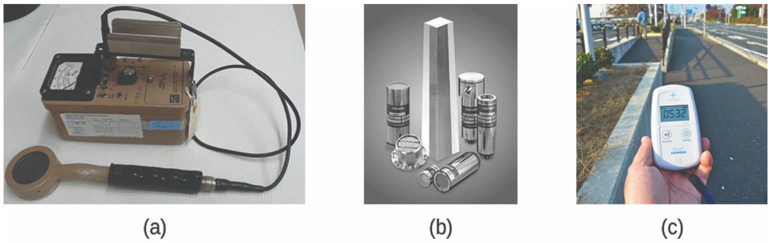

Figure 10.6.6: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (Credit c: modification of work by "osaMu"/Wikimedia commons.)

Three photographs are shown and labeled "a," "b" and "c." Photo a shows a Geiger counter sitting on a table. It is made up of a metal box with a read-out screen and a wire leading away from the box connected to a sensor wand. Photograph b shows a collection of tall and short vertical tubes arranged in a grouping while photograph c shows a person's hand holding a small machine with a digital readout while standing on the edge of a roadway.

A variety of units are used to measure various aspects of radiation (Table $10.6.1$). The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = 3.7×10^{10} disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose.

Table 10.6.1: Units Used for Measuring Radiation

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes 3.7×10^{10} decays/second
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE × Gy
	roentgen equivalent for man (rem)		Rem = RBE × rad

The roentgen equivalent for man (rem) is the unit for radiation damage that is used most frequently in medicine (1 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy), along with a biological factor referred to as the RBE (for relative biological effectiveness), that is an approximate measure of the relative damage done by the radiation. These are related by:

$$\text{number of rems} = \text{RBE} \times \text{number of rads} \tag{10.6.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

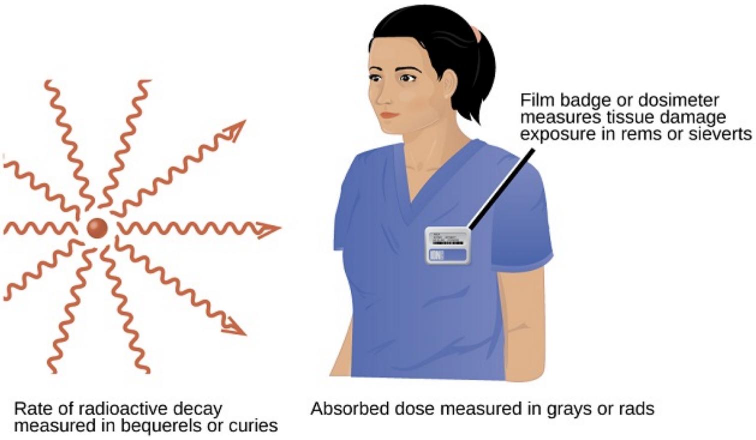

Figure 10.6.7: Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does. (CC by 4.0; OpenStax)

Two images are shown. The first, labeled “Rate of radioactive decay measured in becquerels or curies,” shows a red sphere with ten red squiggly arrows facing away from it in a 360 degree circle. The second image shows the head and torso of a woman wearing medical scrubs with a badge on her chest. The caption to the badge reads “Film badge or dosimeter measures tissue damage exposure in rems or sieverts” while a phrase under this image states “Absorbed dose measured in grays or rads.”

✓ Example 10.6.1: Amount of Radiation

Cobalt-60 ($t_{1/2}$ = 5.26 y) is used in cancer therapy since the γ rays it emits can be focused in small areas where the cancer is located. A 5.00-g sample of Co-60 is available for cancer treatment.

a. What is its activity in Bq?
b. What is its activity in Ci?

Solution

The activity is given by:

$$\text{Activity} = \lambda N = \left(\frac{\ln 2}{t_{1/2}}\right) N = \left(\frac{\ln 2}{5.26\ \text{y}}\right) \times 5.00\ \text{g} = 0.659\ \frac{\text{g}}{\text{y}}\ \text{of}\ {}^{60}\text{Co that decay}$$

And to convert this to decays per second:

$$0.659\ \frac{\text{g}}{\text{y}} \times \frac{\text{y}}{365\ \text{day}} \times \frac{1\ \text{day}}{24\ \text{hours}} \times \frac{1\ \text{h}}{3,600\ \text{s}} \times \frac{1\ \text{mol}}{59.9\ \text{g}} \times \frac{6.02 \times 10^{23}\ \text{atoms}}{1\ \text{mol}} \times \frac{1\ \text{decay}}{1\ \text{atom}}$$

$$= 2.10 \times 10^{14}\ \frac{\text{decay}}{\text{s}}$$

(a) Since $1\ \text{Bq} = 1\ \frac{\text{decay}}{\text{s}}$, the activity in Becquerel (Bq) is:

$$2.10 \times 10^{14}\frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Bq}}{1\ \frac{\text{decay}}{\text{s}}}\right) = 2.10 \times 10^{14}\ \text{Bq}$$

(b) Since $1\ \text{Ci} = 3.7 \times 10^{11}\ \frac{\text{decay}}{\text{s}}$, the activity in curie (Ci) is:

$$2.10 \times 10^{14}\frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Ci}}{3.7 \times 10^{11}\frac{\text{decay}}{\text{s}}}\right) = 5.7 \times 10^{2}\ \text{Ci}$$

? Exercise 10.6.1

Tritium is a radioactive isotope of hydrogen ($t_{1/2} = 12.32$ years) that has several uses, including self-powered lighting, in which electrons emitted in tritium radioactive decay cause phosphorus to glow. Its nucleus contains one proton and two neutrons, and the atomic mass of tritium is 3.016 amu. What is the activity of a sample containing 1.00mg of tritium (a) in Bq and (b) in Ci?

Answer a

$3.56 \times 10^{11} \mathrm{Bq}$

Answer b

0.962 Ci

10.6.4: Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure 10.6.8, the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

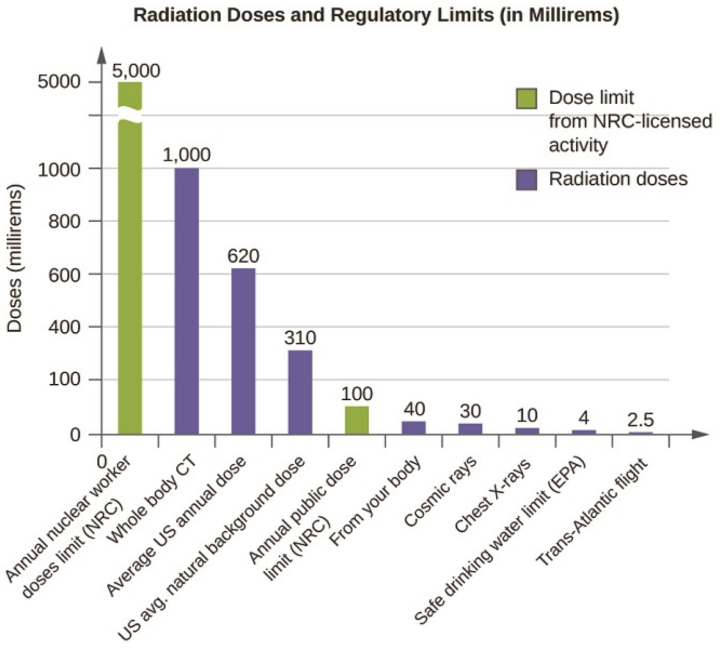

Figure 10.6.8: The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission).

A bar graph titled “Radiation Doses and Regulatory Limits, open parenthesis, in Millirems, close parenthesis” is shown. The y-axis is labeled “Doses in Millirems” and has values from 0 to 5000 with a break between 1000 and 5000 to indicate a different scale to the top of the graph. The y-axis is labeled corresponding to each bar. The first bar, measured to 5000 on the y-axis, is drawn in red and is labeled “Annual Nuclear Worker Doses Limit, open parenthesis, N R C, close parenthesis.” The second bar, measured to 1000 on the y-axis, is drawn in blue and is labeled “Whole Body C T” while the third bar, measured to 620 on the y-axis, is drawn in blue and is labeled “Average U period S period Annual Dose.” The fourth bar, measured to 310 on the y-axis, is drawn in blue and is labeled “U period S period Natural Background Dose” while the fifth bar, measured to 100 on the y-axis and drawn in red reads “Annual Public Dose Limit, open parenthesis, N R C, close parenthesis.” The sixth bar, measured to 40 on the y-axis, is drawn in blue and is labeled “From Your Body” while the seventh bar, measured to 30 on the y-axis and drawn in blue reads “Cosmic rays.” The eighth bar, measured to 4 on the y-axis, is drawn in blue and is labeled “Safe Drinking Water Limit, open parenthesis, E P A, close parenthesis” while the ninth bar, measured to 2.5 on the y-axis and drawn in red reads “Trans Atlantic Flight.” A legend on the graph shows that red means “Dose Limit From N R C dash licensed activity” while blue means “Radiation Doses.”

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person’s lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table 10.6.2.

Table 10.6.2: Health Effects of Radiation

Exposure (rem)	Health Effect	Time to Onset (Without Treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

Summary

We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources. This radiation can affect living organisms. Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes. Radiation can cause somatic or genetic damage, and is most harmful to rapidly reproducing cells. Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating, but potentially most damaging, and gamma rays the most penetrating.

Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure. We use several units to measure radiation: becquerels or curies for rates of radioactive decay; gray or rads for energy absorbed; and rems or sieverts for biological effects of radiation. Exposure to radiation can cause a wide range of health effects, from minor to severe, including death. We can minimize the effects of radiation by shielding with dense materials such as lead, moving away from the source of radiation, and limiting time of exposure.

Footnotes

1. 1 Source: US Environmental Protection Agency

Glossary

becquerel (Bq)

SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s.

curie (Ci)

Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s.

Geiger counter

Instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube.

gray (Gy)

SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue.

ionizing radiation

Radiation that can cause a molecule to lose an electron and form an ion.

millicurie (mCi)

Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s.

nonionizing radiation

Radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules.

radiation absorbed dose (rad)

SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy.

radiation dosimeter

Device that measures ionizing radiation and is used to determine personal radiation exposure.

relative biological effectiveness (RBE)

Measure of the relative damage done by radiation.

roentgen equivalent man (rem)

Unit for radiation damage, frequently used in medicine; 1 rem = 1 Sv.

scintillation counter

Instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation.

sievert (Sv)

SI unit measuring tissue damage caused by radiation; takes energy and biological effects of radiation into account.

10.E: Nuclear Chemistry (Exercises)

10.E.1: **Nuclear Structure and Stability**

1. Write the following isotopes in hyphenated form (e.g., “carbon-14”)

- Na1124
- Al1329
- Kr3673
- Ir77194

2. Write the following isotopes in nuclide notation (e.g., " C614 ")

- oxygen-14
- copper-70
- tantalum-175
- francium-217

3. For the following isotopes that have missing information, fill in the missing information to complete the notation

- X1434
- P36
- MnX57
- X56121

4.For each of the isotopes in teh previous question, determine the numbers of protons, neutrons, and electrons in a neutral atom of the isotope.

5. Write the nuclide notation, including charge if applicable, for atoms with the following characteristics:

- 25 protons, 20 neutrons, 24 electrons
- 45 protons, 24 neutrons, 43 electrons
- 53 protons, 89 neutrons, 54 electrons
- 97 protons, 146 neutrons, 97 electrons

6. Calculate the density of the Mg1224 nucleus in g/mL, assuming that it has the typical nuclear diameter of 1×10^{-13} cm and is spherical in shape.

7. What are the two principal differences between nuclear reactions and ordinary chemical changes?

8. The mass of the atom Na1123Na1123 is 22.9898 amu.

a. Calculate its binding energy per atom in millions of electron volts.

b. Calculate its binding energy per nucleon.

9. Which of the following nuclei lie within the band of stability?

- chlorine-37
- calcium-40
- ^{204}Bi
- ^{56}Fe
- ^{206}Pb
- ^{211}Pb
- ^{222}Rn
- carbon-14

10. Which of the following nuclei lie within the band of stability?

- argon-40
- oxygen-16
- ^{122}Ba
- ^{58}Ni

- ^{205}Tl
- ^{210}Tl
- ^{226}Ra
- magnesium-24

10.E.2: **Nuclear Equations**

11. Write a brief description or definition of each of the following:

- nucleon
- α particle
- β particle
- positron
- γ ray
- nuclide
- mass number
- atomic number

12. Which of the various particles (α particles, β particles, and so on) that may be produced in a nuclear reaction are actually nuclei?

13. Complete each of the following equations by adding the missing species:

- Al1327+He24⟶?+n01
- Pu94239+?⟶Cm96242+n01
- N714+He24⟶?+H11
- U92235⟶?+Cs55135+401n

14. Complete each of the following equations:

- Li37+?⟶224He
- C614⟶N714+?
- Al1327+He24⟶?+n01
- Cm96250⟶?+Sr3898+401n

15. Write a balanced equation for each of the following nuclear reactions:

- the production of ^{17}O from ^{14}N by α particle bombardment
- the production of ^{14}C from ^{14}N by neutron bombardment
- the production of ^{233}Th from ^{232}Th by neutron bombardment
- the production of ^{239}U from ^{238}U by H12H12 bombardment

16. Technetium-99 is prepared from ^{98}Mo. Molybdenum-98 combines with a neutron to give molybdenum-99, an unstable isotope that emits a β particle to yield an excited form of technetium-99, represented as ^{99}Tc*. This excited nucleus relaxes to the ground state, represented as ^{99}Tc, by emitting a γ ray. The ground state of ^{99}Tc then emits a β particle. Write the equations for each of these nuclear reactions.

17. The mass of the atom F919F919 is 18.99840 amu.

- Calculate its binding energy per atom in millions of electron volts.
- Calculate its binding energy per nucleon.

18. For the reaction C614⟶N714+?C614⟶N714+?, if 100.0 g of carbon reacts, what volume of nitrogen gas (N_2) is produced at 273 K and 1 atm?

10.E.3: **Radioactive Decay**

19. What are the types of radiation emitted by the nuclei of radioactive elements?

20. What changes occur to the atomic number and mass of a nucleus during each of the following decay scenarios?

- an α particle is emitted
- a β particle is emitted

- γ radiation is emitted
- a positron is emitted
- an electron is captured

21. What is the change in the nucleus that results from the following decay scenarios?

- emission of a β particle
- emission of a β^+ particle
- capture of an electron

22. any nuclides with atomic numbers greater than 83 decay by processes such as electron emission. Explain the observation that the emissions from these unstable nuclides also normally include α particles.

23. Why is electron capture accompanied by the emission of an X-ray?

24. Explain how unstable heavy nuclides (atomic number > 83) may decompose to form nuclides of greater stability (a) if they are below the band of stability and (b) if they are above the band of stability.

25. Which of the following nuclei is most likely to decay by positron emission? Explain your choice.

- chromium-53
- manganese-51
- iron-59

26. The following nuclei do not lie in the band of stability. How would they be expected to decay? Explain your answer.

- P1534
- U92239
- Ca2038
- H13
- Pu94245

27. The following nuclei do not lie in the band of stability. How would they be expected to decay?

- P1528
- U92235
- 2037Ca
- Li39
- Cm96245

28. Predict by what mode(s) of spontaneous radioactive decay each of the following unstable isotopes might proceed:

- He26
- Zn3060
- Pa91235
- Np94241
- ^{18}F
- ^{129}Ba
- ^{237}Pu

29. Write a nuclear reaction for each step in the formation of Po84218 from U92238, which proceeds by a series of decay reactions involving the step-wise emission of α, β, β, α, α, α, α particles, in that order.

30. Write a nuclear reaction for each step in the formation of Pb82208 from Th90228, which proceeds by a series of decay reactions involving the step-wise emission of α, α, α, α, β, β, α particles, in that order.

31. Define the term half-life and illustrate it with an example.

32. A 1.00×10^{-6}-g sample of nobelium, No102254No102254, has a half-life of 55 seconds after it is formed. What is the percentage of No102254No102254 remaining at the following times?

- 5.0 min after it forms
- 1.0 h after it forms

33. ^{239}Pu is a nuclear waste byproduct with a half-life of 24,000 y. What fraction of the ^{239}Pu present today will be present in 1000 y?

34. The isotope ^{208}Tl undergoes β decay with a half-life of 3.1 min.

- What isotope is produced by the decay?
- How long will it take for 99.0% of a sample of pure ^{208}Tl to decay?
- What percentage of a sample of pure ^{208}Tl remains un-decayed after 1.0 h?

36. If 1.000 g of Ra88226 produces 0.0001 mL of the gas Rn86222 at STP (standard temperature and pressure) in 24 h, what is the half-life of ^{226}Ra in years?

37. The isotope Sr3890 is one of the extremely hazardous species in the residues from nuclear power generation. The strontium in a 0.500-g sample diminishes to 0.393 g in 10.0 y. Calculate the half-life.

38. Technetium-99 is often used for assessing heart, liver, and lung damage because certain technetium compounds are absorbed by damaged tissues. It has a half-life of 6.0 h. Calculate the rate constant for the decay of Tc4399Tc4399.

39. What is the age of mummified primate skin that contains 8.25% of the original quantity of ^{14}C?

40. A sample of rock was found to contain 8.23 mg of rubidium-87 and 0.47 mg of strontium-87.

a. Calculate the age of the rock if the half-life of the decay of rubidium by β emission is 4.7×10^{10} y.

b. If some Sr3887 was initially present in the rock, would the rock be younger, older, or the same age as the age calculated in (a)? Explain your answer.

41. A laboratory investigation shows that a sample of uranium ore contains 5.37 mg of U92238U92238 and 2.52 mg of Pb82206Pb82206. Calculate the age of the ore. The half-life of U92238 is 4.5×10^9 yr.

42. Plutonium was detected in trace amounts in natural uranium deposits by Glenn Seaborg and his associates in 1941. They proposed that the source of this ^{239}Pu was the capture of neutrons by ^{238}U nuclei. Why is this plutonium not likely to have been trapped at the time the solar system formed 4.7×10^9 years ag

43. A Be47 atom (mass = 7.0169 amu) decays into a Li37 atom (mass = 7.0160 amu) by electron capture. How much energy (in millions of electron volts, MeV) is produced by this reaction?

44. A B58 atom (mass = 8.0246 amu) decays into a Be48 atom (mass = 8.0053 amu) by loss of a β^+ particle (mass = 0.00055 amu) or by electron capture. How much energy (in millions of electron volts) is produced by this reaction?

45. Isotopes such as ^{26}Al (half-life: 7.2×10^5 years) are believed to have been present in our solar system as it formed, but have since decayed and are now called extinct nuclides.

a. ^{26}Al decays by β^+ emission or electron capture. Write the equations for these two nuclear transformations.

b. The earth was formed about 4.7×10^9 (4.7 billion) years ago. How old was the earth when 99.999999% of the ^{26}Al originally present had decayed?

46. Write a balanced equation for each of the following nuclear reactions:

- bismuth-212 decays into polonium-212
- beryllium-8 and a positron are produced by the decay of an unstable nucleus
- neptunium-239 forms from the reaction of uranium-238 with a neutron and then spontaneously converts into plutonium-239
- strontium-90 decays into yttrium-90

47. Write a balanced equation for each of the following nuclear reactions:

- mercury-180 decays into platinum-176
- zirconium-90 and an electron are produced by the decay of an unstable nucleus
- thorium-232 decays and produces an alpha particle and a radium-228 nucleus, which decays into actinium-228 by beta decay
- neon-19 decays into fluorine-19

10.E.4: **Transmutation and Nuclear Energy**

48. Write the balanced nuclear equation for the production of the following transuranium elements:

- berkelium-244, made by the reaction of Am-241 and He-4
- fermium-254, made by the reaction of Pu-239 with a large number of neutrons
- lawrencium-257, made by the reaction of Cf-250 and B-11
- dubnium-260, made by the reaction of Cf-249 and N-15

49. How does nuclear fission differ from nuclear fusion? Why are both of these processes exothermic?

50. Both fusion and fission are nuclear reactions. Why is a very high temperature required for fusion, but not for fission?

51. Cite the conditions necessary for a nuclear chain reaction to take place. Explain how it can be controlled to produce energy, but not produce an explosion.

52. Describe the components of a nuclear reactor.

53. In usual practice, both a moderator and control rods are necessary to operate a nuclear chain reaction safely for the purpose of energy production. Cite the function of each and explain why both are necessary.

54. Describe how the potential energy of uranium is converted into electrical energy in a nuclear power plant.

55. The mass of a hydrogen atom (11H) is 1.007825 amu; that of a tritium atom (13H) is 3.01605 amu; and that of an α particle is 4.00150 amu. How much energy in kilojoules per mole of He24 produced is released by the following fusion reaction: H11+H13⟶He24.

10.E.5: **Uses of Radioisotopes**

56. How can a radioactive nuclide be used to show that the equilibrium:

AgCl(s)⇌Ag+(aq)+Cl−(aq)

is a dynamic equilibrium?

57. Technetium-99m has a half-life of 6.01 hours. If a patient injected with technetium-99m is safe to leave the hospital once 75% of the dose has decayed, when is the patient allowed to leave?

58. Iodine that enters the body is stored in the thyroid gland from which it is released to control growth and metabolism. The thyroid can be imaged if iodine-131 is injected into the body. In larger doses, I-131 is also used as a means of treating cancer of the thyroid. I-131 has a half-life of 8.70 days and decays by β^- emission.

1. Write a nuclear equation for the decay.
2. How long will it take for 95.0% of a dose of I-131 to decay?

10.E.6: **Biological Effects of Radiation**

59. If a hospital were storing radioisotopes, what is the minimum containment needed to protect against:

- cobalt-60 (a strong γ emitter used for irradiation)
- molybdenum-99 (a beta emitter used to produce technetium-99 for imaging)

60. Based on what is known about Radon-222’s primary decay method, why is inhalation so dangerous?

61. Given specimens uranium-232 (t1/2=68.9yt1/2=68.9y) and uranium-233 (t1/2=159,200yt1/2=159,200y) of equal mass, which one would have greater activity and why?

62. A scientist is studying a 2.234 g sample of thorium-229 ($t_{1/2}$ = 7340 y) in a laboratory.

- What is its activity in Bq?
- What is its activity in Ci?

63. Given specimens neon-24 (t1/2=3.38mint1/2=3.38min) and bismuth-211 (t1/2=2.14mint1/2=2.14min) of equal mass, which one would have greater activity and why?

Index

Glossary

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        - 2.7: Transition Metals and Coordination Chemistry (Exercises) - *CC BY 4.0*
    - 3: Chemical Kinetics - *Undeclared*
        - 3.1: Chemical Reaction Rates - *CC BY 4.0*
        - 3.2: Factors Affecting Reaction Rates - *CC BY 4.0*
        - 3.3: Rate Laws - *CC BY 4.0*
        - 3.4: Integrated Rate Laws - *CC BY 4.0*
        - 3.5: Collision Theory - *CC BY 4.0*
        - 3.6: Reaction Mechanisms - *CC BY 4.0*
        - 3.7: Catalysis - *CC BY 4.0*
        - 3.E: Kinetics (Exercises) - *CC BY 4.0*
    - 4: Chemical Equilibrium - *Undeclared*
        - 4.1: Chemical Equilibria - *CC BY 4.0*
        - 4.2: Equilibrium Constants - *CC BY 4.0*
        - 4.3: Gas Phase Equilibria and Heterogeneous Systems - *CC BY-NC-SA 4.0*
        - 4.4: Shifting Equilibria - Le Chatelier’s Principle - *CC BY 4.0*
        - 4.5: Calculating Equilibrium Constants and Equilibrium Concentrations - *CC BY-NC-SA 4.0*
        - 4.6: Calculating Equilibrium Concentrations with the "x-is-small" Approximation - *CC BY 4.0*
        - 4.7: Equilibrium Constant Manipulations - *Undeclared*
        - 4.E: Fundamental Equilibrium Concepts (Exercises) - *CC BY 4.0*
    - 5: Acid-Base Equilibria - *Undeclared*
        - 5.1: Brønsted-Lowry Acids and Bases - *CC BY 4.0*
        - 5.2: pH and pOH - *CC BY 4.0*
        - 5.3: Relative Strengths of Acids - *CC BY 4.0*
        - 5.4: pH Calculations for Weak Acids - *CC BY 4.0*
        - 5.5: Relative Strengths of Bases - *CC BY 4.0*
        - 5.6: Relating Structure to Acidity and Basicity - *CC BY 4.0*
        - 5.7: Hydrolysis of Salt Solutions - *CC BY 4.0*

  - 5.E: Acid-Base Equilibria (Exercises) - *CC BY 4.0*
- 6: Acid-Base Equilibria in Mixtures - *CC BY 4.0*
  - 6.1: Mixtures of Acids - *Undeclared*
  - 6.2: Polyprotic Acids - *CC BY 4.0*
  - 6.3: Buffers - *CC BY 4.0*
  - 6.4: Henderson-Hasselbalch Approximation - *Undeclared*
  - 6.5: Acid-Base Titrations - *CC BY 4.0*
  - 6.6: pH Calculations for Acid–Base Titrations - *CC BY-NC-SA 4.0*
  - 6.E: Acid-Base Equilibria (Exercises) - *CC BY 4.0*
- 7: Solubility and Complex-Ion Equilibria - *Undeclared*
  - 7.1: Solubility Product Constant, Ksp - *Undeclared*
  - 7.2: Relationship Between Solubility and Ksp - *CC BY 4.0*
  - 7.3: Common-Ion Effect in Solubility Equilibria - *Undeclared*
  - 7.4: Criteria for Precipitation and its Completeness - *Undeclared*
  - 7.5: Fractional Precipitation - *Undeclared*
  - 7.6: Solubility and pH - *CC BY-NC-SA 4.0*
  - 7.7: Equilibria Involving Complex Ions - *Undeclared*
  - 7.8: Qualitative Cation Analysis - *Undeclared*
  - 7.9: Equilibria of Other Reaction Classes (Exercises) - *CC BY 4.0*
- 8: Thermodynamics - *Undeclared*
  - 8.1: Spontaneity- The Meaning of Spontaneous Change - *CC BY 4.0*
  - 8.2: The Concept of Entropy - *Undeclared*
  - 8.3: Evaluating Entropy and Entropy Changes - *Undeclared*
  - 8.4: Criteria for Spontaneous Change- The Second Law of Thermodynamics - *Undeclared*
  - 8.5: Standard Gibbs Energy Change, ΔG° - *Undeclared*
  - 8.6: Gibbs Energy Change and Equilibrium - *Undeclared*
  - 8.7: ΔG° and K as Functions of Temperature - *Undeclared*
  - 8.8: Coupled Reactions - *Undeclared*
  - 8.E: Chemical Thermodynamics (Exercises) - *Undeclared*
- 9: Electrochemistry - *CC BY 4.0*
  - 9.1: Balancing Oxidation-Reduction Reactions - *CC BY 4.0*
  - 9.2: Galvanic Cells - *CC BY 4.0*
  - 9.3: Standard Reduction Potentials - *CC BY 4.0*
  - 9.4: The Nernst Equation - *CC BY 4.0*
  - 9.5: Batteries and Fuel Cells - *CC BY 4.0*
  - 9.6: Corrosion - *CC BY 4.0*
  - 9.7: Electrolysis - *CC BY 4.0*
  - 9.E: Electrochemistry (Exercises) - *CC BY 4.0*
- 10: Nuclear Chemistry - *CC BY 4.0*
  - 10.1: Nuclear Equations - *CC BY 4.0*
  - 10.2: Radioactive Decay - *CC BY 4.0*
  - 10.3: Nuclear Structure and Stability - *CC BY 4.0*
  - 10.4: Transmutation and Nuclear Energy - *CC BY 4.0*
  - 10.5: Uses of Radioisotopes - *CC BY 4.0*
  - 10.6: Biological Effects of Radiation - *CC BY 4.0*
  - 10.E: Nuclear Chemistry (Exercises) - *CC BY 4.0*
- Back Matter - *Undeclared*
  - Index - *Undeclared*
  - Glossary - *Undeclared*
  - Detailed Licensing - *Undeclared*