CHEM 2141: SURVEY OF PHYSICAL CHEMISTRY

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CHEM 2141: Survey of Physical Chemistry

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TABLE OF CONTENTS

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CHAPTER OVERVIEW

1: Introduction

Thermodynamics is a quantitative subject. It allows us to derive relations between the values of numerous physical quantities. Some physical quantities, such as a mole fraction, are dimensionless; the value of one of these quantities is a pure number. Most quantities, however, are not dimensionless and their values must include one or more *units*. This chapter reviews the SI system of units, which are the preferred units in science applications. The chapter then discusses some useful mathematical manipulations of physical quantities using quantity calculus, and certain general aspects of dimensional analysis.

1.1: Units

There is international agreement that the units used for physical quantities in science and technology should be those of the International System of Units, or SI (standing for the French **Système International d'Unités**). The Physical Chemistry Division of the International Union of Pure and Applied Chemistry, or IUPAC, produces a manual of recommended symbols and terminology for physical quantities and units based on the SI. The manual has become known as the Green Book (from the color of its cover) and is referred to here as the IUPAC Green Book. This e-book will, with a few exceptions, use symbols recommended in the third edition (2007) of the IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition. RSC Publishing, Cambridge, 2007). These symbols are listed for convenient reference in Appendices C and D.

Any of the symbols for units listed in Tables 1.1–1.3, except kg and $^{\circ}\mathrm{C}$, may be preceded by one of the prefix symbols of Table 1.4 to construct a decimal fraction or multiple of the unit. (The symbol g may be preceded by a prefix symbol to construct a fraction or multiple of the gram.) The combination of prefix symbol and unit symbol is taken as a new symbol that can be raised to a power without using parentheses, as in the following examples:

- The physical quantity formally called **amount of substance** is a counting quantity for particles, such as atoms or molecules, or for other chemical entities. The counting unit is invariably the **mole**, defined as the amount of substance containing as many particles as the number of atoms in exactly 12 grams of pure carbon-12 nuclide, $^{12}\mathrm{C}$. See Appendix A for the wording of the official IUPAC definition. This definition is such that one mole of $\mathrm{H_2O}$ molecules, for example, has a mass of 18.0153 grams (where 18.0153 is the relative molecular mass of $\mathrm{H_2O}$) and contains 6.02214×10^{23} molecules (where $6.02214 \times 10^{23}\ \mathrm{mol^{-1}}$ is the *Avogadro constant* to six significant digits). The same statement can be made for any other substance if 18.0153 is replaced by the appropriate atomic mass or molecular mass value.

  The symbol for amount of substance is n. It is admittedly awkward to refer to $n(\mathrm{H_2O})$ as "the amount of substance of water." This e-book simply shortens "amount of substance" to **amount**. An alternative name suggested for n is "chemical amount." Thus, "the amount of water in the system" refers not to the mass or volume of water, but to the *number* of $\mathrm{H_2O}$ molecules in the system expressed in a counting unit such as the mole.
-

1.2: Quantity Calculus

This section gives examples of how we may manipulate physical quantities by the rules of algebra. The method is called *quantity calculus*, although a better term might be “quantity algebra.”

This shows the new text

Quantity calculus is based on the concept that a physical quantity, unless it is dimensionless, has a value equal to the product of a *numerical value* (a pure number) and one or more *units*:

$$\text{physical quantity} = \text{numerical value} \times \text{units} \tag{1.2.1}$$

(If the quantity is dimensionless, it is equal to a pure number without units.) The physical property may be denoted by a symbol, but the symbol does *not* imply a particular choice of units. For instance, this e-book uses the symbol ρ for density, but ρ can be expressed in any units having the dimensions of mass divided by volume.

A simple example illustrates the use of quantity calculus. We may express the density of water at $25\,^{\circ}\mathrm{C}$ to four significant digits in SI base units by the equation

$$\rho = 9.970 \times 10^2 \text{ kg m}^{-3} \tag{1.2.2}$$

and in different density units by the equation

$$\rho = 0.9970\,\text{g cm}^{-3} \tag{1.2.3}$$

We may divide both sides of the last equation by 1 g cm^{-3} to obtain a new equation

$$\rho/\text{g cm}^{-3} = 0.9970 \tag{1.2.4}$$

Now the pure number 0.9970 appearing in this equation is the number of grams in one cubic centimeter of water, so we may call the ratio $\rho/\text{g cm}^{-3}$ “the number of grams per cubic centimeter.” By the same reasoning, $\rho/\text{kg m}^{-3}$ is the number of kilograms per cubic meter. In general, a physical quantity divided by particular units for the physical quantity is a pure number representing the number of those units.

> Just as it would be incorrect to call ρ “the number of grams per cubic centimeter,” because that would refer to a particular choice of units for ρ, the common practice of calling n “the number of moles” is also strictly speaking not correct. It is actually the ratio n/mol that is the number of moles.

In a table, the ratio $\rho/\text{g cm}^{-3}$ makes a convenient heading for a column of density values because the column can then show pure numbers. Likewise, it is convenient to use $\rho/\text{g cm}^{-3}$ as the label of a graph axis and to show pure numbers at the grid marks of the axis. You will see many examples of this usage in the tables and figures in this e-book.

A major advantage of using SI base units and SI derived units is that they are *coherent*. That is, values of a physical quantity expressed in different combinations of these units have the same numerical value.

For example, suppose we wish to evaluate the pressure of a gas according to the ideal gas equation

$$p = \frac{nRT}{V} \tag{1.2.5}$$

(ideal gas)

This is the first equation that, like many others to follow, shows *conditions of validity* in parentheses immediately below the equation number at the right. Thus, Eq. 1.2.5 is valid for an ideal gas. In this equation, p, n, T, and V are the symbols for the physical quantities pressure, amount (amount of substance), thermodynamic temperature, and volume, respectively, and R is the gas constant.

The calculation of p for 5.000 moles of an ideal gas at a temperature of 298.15 kelvins, in a volume of 4.000 cubic meters, is

$$p = \frac{(5.000\,\text{mol})(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}{4.000\,\text{m}^3} = 3.099 \times 10^3 \text{ J m}^{-3} \tag{1.2.6}$$

The mole and kelvin units cancel, and we are left with units of J m^{-3}, a combination of an SI derived unit (the joule) and an SI base unit (the meter). The units J m^{-3} must have dimensions of pressure, but are not commonly used to express pressure.

To convert J m^{-3} to the SI derived unit of pressure, the pascal (Pa), we can use the following relations from Table 1.2:

$$1\,\mathrm{J}=1\,\mathrm{N\,m} \qquad 1\,\mathrm{Pa}=1\,\mathrm{N\,m^{-2}} \tag{1.2.7}$$

When we divide both sides of the first relation by $1\,\mathrm{J}$ and divide both sides of the second relation by $1\,\mathrm{N\,m^{-2}}$, we obtain the two new relations

$$1=(1\,\mathrm{N\,m/J}) \qquad (1\,\mathrm{Pa/N\,m^{-2}})=1 \tag{1.2.8}$$

The ratios in parentheses are *conversion factors*. When a physical quantity is multiplied by a conversion factor that, like these, is equal to the pure number 1, the physical quantity changes its units but not its value. When we multiply Eq. 1.2.6 by both of these conversion factors, all units cancel except Pa:

$$p\;=(3.099\times 10^3\,\mathrm{J\,m^{-3}})\times(1\,\mathrm{N\,m/J})\times(1\,\mathrm{Pa/N\,m^{-2}})\;=3.099\times 10^3\,\mathrm{Pa} \tag{1.2.9}$$

This example illustrates the fact that to calculate a physical quantity, we can simply enter into a calculator numerical values expressed in SI units, and the result is the numerical value of the calculated quantity expressed in SI units. In other words, as long as we use only SI base units and SI derived units (without prefixes), *all conversion factors are unity*.

Of course we do not have to limit the calculation to SI units. Suppose we wish to express the calculated pressure in torrs, a non-SI unit. In this case, using a conversion factor obtained from the definition of the torr in Table 1.3, the calculation becomes

$$p\;=(3.099\times 10^3\,\mathrm{Pa})\times(760\,\mathrm{Torr}/101,325\,\mathrm{Pa})=23.24\,\mathrm{Torr} \tag{1.2.10}$$

1.3: Dimensional Analysis

Sometimes you can catch an error in the form of an equation or expression, or in the dimensions of a quantity used for a calculation, by checking for dimensional consistency. Here are some rules that must be satisfied:

- In this e-book the *differential* of a function, such as $\mathrm{d}f$, refers to an *infinitesimal* quantity. If one side of an equation is an infinitesimal quantity, the other side must also be. Thus, the equation $\mathrm{d}f = a\,\mathrm{d}x + b\,\mathrm{d}y$ (where ax and by have the same dimensions as f) makes mathematical sense, but $\mathrm{d}f = ax + b\,\mathrm{d}y$ does not.

  Derivatives, partial derivatives, and integrals have dimensions that we must take into account when determining the overall dimensions of an expression that includes them. For instance:

  - Some examples of applying these principles are given here using symbols described in Sec. 1.2.

    Example 1. Since the gas constant R may be expressed in units of $\mathrm{J\ K^{-1}\ mol^{-1}}$, it has dimensions of energy divided by thermodynamic temperature and amount. Thus, RT has dimensions of energy divided by amount, and nRT has dimensions of energy. The products RT and nRT appear frequently in thermodynamic expressions.

    Example 3. Find the dimensions of the constants a and b in the van der Waals equation

    $$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \tag{1.3.1}$$

    Dimensional analysis tells us that, because nb is subtracted from V, nb has dimensions of volume and therefore b has dimensions of volume/amount. Furthermore, since the right side of the equation is a difference of two terms, these terms have the same dimensions as the left side, which is pressure. Therefore, the second term n^2a/V^2 has dimensions of pressure, and a has dimensions of pressure $\times$ volume^2 $\times$ amount^{-2}.

    Example 4. Consider an equation of the form

    $$\left(\frac{\partial \ln x}{\partial T}\right)_p = \frac{y}{R} \tag{1.3.2}$$

    What are the SI units of y? $\ln x$ is dimensionless, so the left side of the equation has the dimensions of $1/T$, and its SI units are $\mathrm{K^{-1}}$. The SI units of the right side are therefore also $\mathrm{K^{-1}}$. Since R has the units $\mathrm{J\ K^{-1}\ mol^{-1}}$, the SI units of y are $\mathrm{J\ K^{-2}\ mol^{-1}}$.

1.4: Chapter 1 Problem

1.1

Consider the following equations for the pressure of a real gas. For each equation, find the dimensions of the constants a and b and express these dimensions in SI units.

(a) The Dieterici equation:

$$p = \frac{RTe^{-(an/VRT)}}{(V/n) - b} \tag{1.4.1}$$

(b) The Redlich–Kwong equation:

$$p = \frac{RT}{(V/n) - b} - \frac{an^2}{T^{1/2}V(V + nb)} \tag{1.4.2}$$

CHAPTER OVERVIEW

2: General Chemistry Review

SECTION OVERVIEW

2.1: Gases

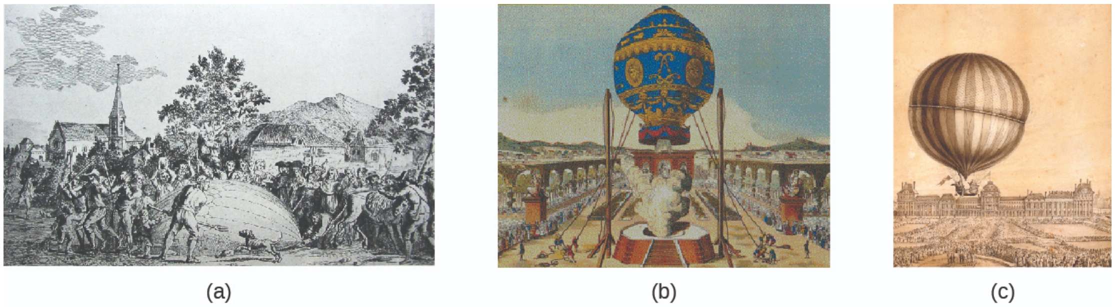
2.1.1: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

Learning Objectives

By the end of this section, you will be able to:

- Identify the mathematical relationships between the various properties of gases
- Use the ideal gas law, and related gas laws, to compute the values of various gas properties under specified conditions

During the seventeenth and especially eighteenth centuries, driven both by a desire to understand nature and a quest to make balloons in which they could fly (Figure 2.1.1.1), a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, volume, temperature, and amount of gas. Although their measurements were not precise by today's standards, they were able to determine the mathematical relationships between pairs of these variables (e.g., pressure and temperature, pressure and volume) that hold for an *ideal* gas—a hypothetical construct that real gases approximate under certain conditions. Eventually, these individual laws were combined into a single equation—the *ideal gas law*—that relates gas quantities for gases and is quite accurate for low pressures and moderate temperatures. We will consider the key developments in individual relationships (for pedagogical reasons not quite in historical order), then put them together in the ideal gas law.



(a) (b) (c)

Figure 2.1.1.1: In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris.

Pressure and Temperature: Amontons's Law

Imagine filling a rigid container attached to a pressure gauge with gas and then sealing the container so that no gas may escape. If the container is cooled, the gas inside likewise gets colder and its pressure is observed to decrease. Since the container is rigid and tightly sealed, both the volume and number of moles of gas remain constant. If we heat the sphere, the gas inside gets hotter (Figure 2.1.1.2) and the pressure increases.

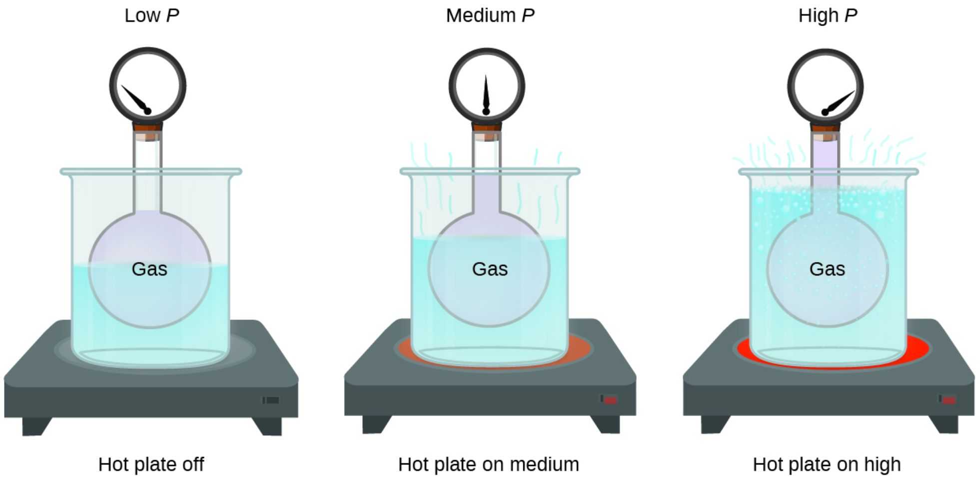


Figure 2.1.1.2: The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases.

This relationship between temperature and pressure is observed for any sample of gas confined to a constant volume. An example of experimental pressure-temperature data is shown for a sample of air under these conditions in Figure $2.1.1.3$. We find that temperature and pressure are linearly related, and if the temperature is on the kelvin scale, then P and T are directly proportional (again, when *volume and moles of gas are held constant*); if the temperature on the kelvin scale increases by a certain factor, the gas pressure increases by the same factor.

Temperature (°C)	Temperature (K)	Pressure (kPa)
−100	173	36.0
−50	223	46.4
0	273	56.7
50	323	67.1
100	373	77.5
150	423	88.0

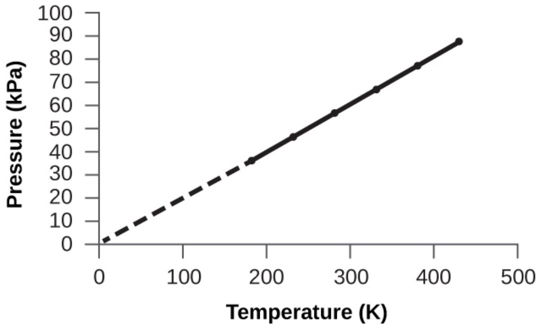


Figure $2.1.1.3$: For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at –273 °C, which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero.

Guillaume Amontons was the first to empirically establish the relationship between the pressure and the temperature of a gas (~1700), and Joseph Louis Gay-Lussac determined the relationship more precisely (~1800). Because of this, the P-T relationship for gases is known as either **Amontons's law** or **Gay-Lussac's law**. Under either name, it states that *the pressure of a given amount of gas is directly proportional to its temperature on the kelvin scale when the volume is held constant*. Mathematically, this can be written:

$$P \propto T \text{ or } P = \text{ constant } \times T \text{ or } P = k \times T$$

where $\propto$ means "is proportional to," and k is a proportionality constant that depends on the identity, amount, and volume of the gas.

For a confined, constant volume of gas, the $\frac{P}{T}$ ratio is therefore constant (i.e., $\frac{P}{T} = k$). If the gas is initially in "Condition 1" (with $P = P_1$ and $T = T_1$), and then changes to "Condition 2" (with $P = P_2$ and $T = T_2$), we have that $\frac{P_1}{T_1} = k$ and $\frac{P_2}{T_2} = k$ which reduces to

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}.$$

This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be on the kelvin scale for any gas law calculations (0 on the kelvin scale and the lowest possible temperature is called **absolute zero**). (Also note that there are at least three ways we can describe how the pressure of a gas changes as its temperature changes: We can use a table of values, a graph, or a mathematical equation.)

✓ Example $2.1.1.1$: Predicting Change in Pressure with Temperature

A can of hair spray is used until it is empty except for the propellant, isobutane gas.

a. On the can is the warning "Store only at temperatures below 120 °F (48.8 °C). Do not incinerate." Why?
b. The gas in the can is initially at 24 °C and 360 kPa, and the can has a volume of 350 mL. If the can is left in a car that reaches 50 °C on a hot day, what is the new pressure in the can?

Solution

(a) The can contains an amount of isobutane gas at a constant volume, so if the temperature is increased by heating, the pressure will increase proportionately. High temperature could lead to high pressure, causing the can to burst. (Also, isobutane is combustible, so incineration could cause the can to explode.)

(b) We are looking for a pressure change due to a temperature change at constant volume, so we will use Amontons's/Gay-Lussac's law. Taking P_1 and T_1 as the initial values, T_2 as the temperature where the pressure is unknown and P_2 as the unknown pressure, and converting °C to K, we have:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ which means that } \frac{360 \text{ kPa}}{297 \text{ K}} = \frac{P_2}{323 \text{ K}}$$

Rearranging and solving gives:

$$P_2 = \frac{360 \text{ kPa} \times 323 \cancel{\text{K}}}{297 \cancel{\text{K}}} = 390 \text{ kPa}$$

? Exercise 2.1.1.1

A sample of nitrogen, N_2, occupies 45.0 mL at 27 °C and 600 torr. What pressure will it have if cooled to –73 °C while the volume remains constant?

Answer

400 torr

Volume and Temperature: Charles's Law

If we fill a balloon with air and seal it, the balloon contains a specific amount of air at atmospheric pressure, let's say 1 atm. If we put the balloon in a refrigerator, the gas inside gets cold and the balloon shrinks (although both the amount of gas and its pressure remain constant). If we make the balloon very cold, it will shrink a great deal, and it expands again when it warms up.

Link to Learning

This video shows how cooling and heating a gas causes its volume to decrease or increase, respectively.

These examples of the effect of temperature on the volume of a given amount of a confined gas at constant pressure are true in general: The volume increases as the temperature increases, and decreases as the temperature decreases. Volume-temperature data for a 1-mole sample of methane gas at 1 atm are listed and graphed in Figure 9.12.

Temperature (°C)	Temperature (K)	Volume (L)
–3	270	22
–23	250	21
–53	220	18
–162	111	9

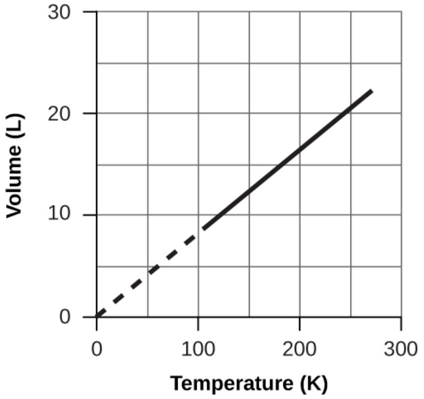


Figure 9.12 The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero.

The relationship between the volume and temperature of a given amount of gas at constant pressure is known as Charles's law in recognition of the French scientist and balloon flight pioneer Jacques Alexandre César Charles. **Charles's law** states that *the volume of a given amount of gas is directly proportional to its temperature on the kelvin scale when the pressure is held constant*.

Mathematically, this can be written as:

$$V \alpha T \text{ or } V = \text{ constant } \cdot T \text{ or } V = k \cdot T \text{ or } V_1/T_1 = V_2/T_2$$

with k being a proportionality constant that depends on the amount and pressure of the gas.

For a confined, constant pressure gas sample, $\frac{V}{T}$ is constant (i.e., the ratio = k), and as seen with the *P*-*T* relationship, this leads to another form of Charles's law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}. \tag{2.1.1.1}$$

Example 2.1.1.2: Predicting Change in Volume with Temperature

A sample of carbon dioxide, CO_2, occupies 0.300 L at 10 °C and 750 torr. What volume will the gas have at 30 °C and 750 torr?

Solution

Because we are looking for the volume change caused by a temperature change at constant pressure, this is a job for Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{0.300 L}{283 K} = \frac{V_2}{303 K}$$

Rearranging and solving gives:

$$V_2 = \frac{0.300 L \times 303 \ \cancel{K}}{283 \ \cancel{K}} = 0.321 \text{ L}$$

This answer supports our expectation from Charles's law, namely, that raising the gas temperature (from 283 K to 303 K) at a constant pressure will yield an increase in its volume (from 0.300 L to 0.321 L).

Exercise 2.1.1.2

A sample of oxygen, O_2, occupies 32.2 mL at 30 °C and 452 torr. What volume will it occupy at –70 °C and the same pressure?

Answer

21.6 mL

Example 2.1.1.3: Measuring Temperature with a Volume Change

Temperature is sometimes measured with a gas thermometer by observing the change in the volume of the gas as the temperature changes at constant pressure. The hydrogen in a particular hydrogen gas thermometer has a volume of 150.0 cm^3 when immersed in a mixture of ice and water (0.00 °C). When immersed in boiling liquid ammonia, the volume of the hydrogen, at the same pressure, is 131.7 cm^3. Find the temperature of boiling ammonia on the kelvin and Celsius scales.

Solution

A volume change caused by a temperature change at constant pressure means we should use Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{150.0 cm^3}{273.15 K} = \frac{131.7 cm^3}{T_2}$$

Rearrangement gives

$$T_2 = \frac{131.7 \ \cancel{cm^3} \times 273.15 \text{ K}}{150.0 \ \cancel{cm^3}} = 239.8 \text{ K}$$

Subtracting 273.15 from 239.8 K, we find that the temperature of the boiling ammonia on the Celsius scale is –33.4 °C.

? Exercise 2.1.1.3

What is the volume of a sample of ethane at 467 K and 1.1 atm if it occupies 405 mL at 298 K and 1.1 atm?

Answer

635 mL

Volume and Pressure: Boyle’s Law

If we partially fill an airtight syringe with air, the syringe contains a specific amount of air at constant temperature, say 25 °C. If we slowly push in the plunger while keeping temperature constant, the gas in the syringe is compressed into a smaller volume and its pressure increases; if we pull out the plunger, the volume increases and the pressure decreases. This example of the effect of volume on the pressure of a given amount of a confined gas is true in general. Decreasing the volume of a contained gas will increase its pressure, and increasing its volume will decrease its pressure. In fact, if the volume increases by a certain factor, the pressure decreases by the same factor, and vice versa. Volume-pressure data for an air sample at room temperature are graphed in Figure 2.1.1.4

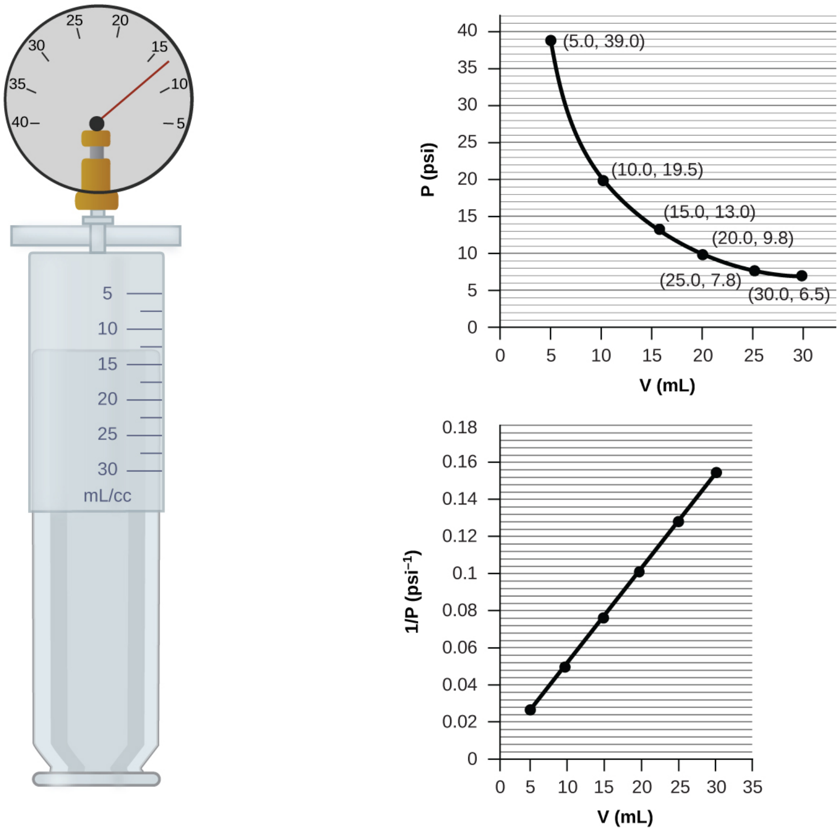


Figure 2.1.1.4: When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since P and V are inversely proportional, a graph of $\frac{1}{P}$ vs. V is linear.

Unlike the P-T and V-T relationships, pressure and volume are not directly proportional to each other. Instead, P and V exhibit inverse proportionality: Increasing the pressure results in a decrease of the volume of the gas. Mathematically this can be written:

$$P \propto \frac{1}{V} \tag{2.1.1.2}$$

or

$$P = k \cdot \frac{1}{V} \tag{2.1.1.3}$$

or

$$P \cdot V = k \tag{2.1.1.4}$$

or

$$P_1V_1 = P_2V_2 \tag{2.1.1.5}$$

with *k* being a constant. Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure

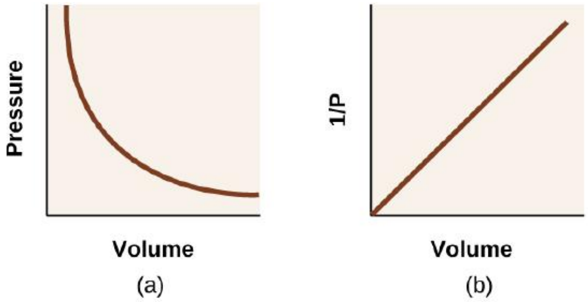


Figure 2.1.1.5: The relationship between pressure and volume is inversely proportional. (a) The graph of *P* vs. *V* is a hyperbola, whereas (b) the graph of $\frac{1}{P}$ vs. *V* is linear.

The relationship between the volume and pressure of a given amount of gas at constant temperature was first published by the English natural philosopher Robert Boyle over 300 years ago. It is summarized in the statement now known as **Boyle's law**: *The volume of a given amount of gas held at constant temperature is inversely proportional to the pressure under which it is measured.*

✓ Example 2.1.1.4: Volume of a Gas Sample

The sample of gas in Figure 2.1.1.4 has a volume of 15.0 mL at a pressure of 13.0 psi. Determine the pressure of the gas at a volume of 7.5 mL, using:

a. the *P*-*V* graph in Figure 2.1.1.5
b. the $\frac{1}{P}$ vs. V graph in Figure 2.1.1.5
c. the Boyle's law equations (Equations 2.1.1.2- 2.1.1.5)

Comment on the likely accuracy of each method.

Solution

(a) Estimating from the *P*-*V* graph gives a value for *P* somewhere around 27 psi.

(b) Estimating from the \frac{1}{P}\) versus V graph give a value of about 26 psi.

(c) From Boyle's law, we know that the product of pressure and volume (*PV*) for a given sample of gas at a constant temperature is always equal to the same value. Therefore we have $P_1V_1 = k$ and $P_2V_2 = k$ which means that $P_1V_1 = P_2V_2$.

Using P_1 and V_1 as the known values 13.0 psi and 15.0 mL, P_2 as the pressure at which the volume is unknown, and V_2 as the unknown volume, we have:

$$P_1\,V_1 = P_2\,V_2$$
$$(13.0\text{ psi}) \times (15.0\text{ mL} = P_2 \times (7.5\text{ mL})$$

Solving:

$$P_2 = \frac{13.0\text{ psi} \times 15.0\ \cancel{\text{mL}}}{7.5\ \cancel{\text{mL}}} = 26\text{ psi}$$

It was more difficult to estimate well from the *P*-*V* graph, so (a) is likely more inaccurate than (b) or (c). The calculation will be as accurate as the equation and measurements allow.

? Exercise 2.1.1.4

The sample of gas in Figure 2.1.1.4 has a volume of 30.0 mL at a pressure of 6.5 psi. Determine the volume of the gas at a pressure of 11.0 psi, using:

a. the *P*-*V* graph in Figure 2.1.1.5
b. the $\frac{1}{P}$ vs. \(*V*\) graph in Figure 2.1.1.5
c. the Boyle's law equations (2.1.1.2- 2.1.1.5)

Comment on the likely accuracy of each method.

Answer

(a) about 17–18 mL; (b) ~18 mL; (c) 17.7 mL; it was more difficult to estimate well from the *P*-*V* graph, so (a) is likely more inaccurate than (b); the calculation will be as accurate as the equation and measurements allow

Chemistry in Everyday Life: Breathing and Boyle's Law

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life (Figure 2.1.1.6).

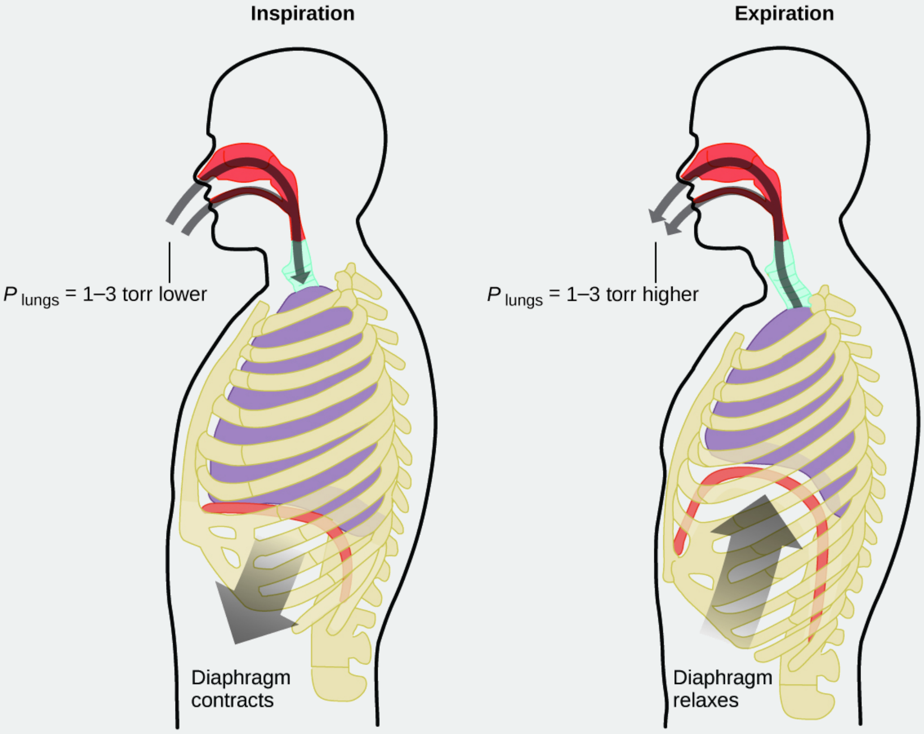


Figure 2.1.1.6: Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.

Moles of Gas and Volume: Avogadro’s Law

The Italian scientist Amedeo Avogadro advanced a hypothesis in 1811 to account for the behavior of gases, stating that equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules. Over time, this relationship was supported by many experimental observations as expressed by **Avogadro’s law**: *For a confined gas, the volume (V) and number of moles (n) are directly proportional if the pressure and temperature both remain constant.*

In equation form, this is written as:

$$V \propto n \tag{2.1.1.6}$$

or

$$V = k \times n \tag{2.1.1.7}$$

or

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \tag{2.1.1.8}$$

Mathematical relationships can also be determined for the other variable pairs, such as P versus n, and n versus T.

Link to Learning

Visit this interactive PhET simulation to investigate the relationships between pressure, volume, temperature, and amount of gas. Use the simulation to examine the effect of changing one parameter on another while holding the other parameters constant (as described in the preceding sections on the various gas laws).

The Ideal Gas Law

To this point, four separate laws have been discussed that relate pressure, volume, temperature, and the number of moles of the gas:

- Boyle’s law: PV = constant at constant T and n
- Amontons’s law: $\frac{P}{T}$ = constant at constant V and n
- Charles’s law: $\frac{V}{T}$ = constant at constant P and n
- Avogadro’s law: $\frac{V}{n}$ = constant at constant P and T

Combining these four laws yields the **ideal gas law**, a relation between the pressure, volume, temperature, and number of moles of a gas:

$$PV = nRT$$

where P is the pressure of a gas, V is its volume, n is the number of moles of the gas, T is its temperature on the kelvin scale, and R is a constant called the **ideal gas constant** or the universal gas constant. The units used to express pressure, volume, and temperature will determine the proper form of the gas constant as required by dimensional analysis, the most commonly encountered values being 0.08206 L atm mol^{-1} K^{-1} and 8.314 kPa L mol^{-1} K^{-1}.

Gases whose properties of P, V, and T are accurately described by the ideal gas law (or the other gas laws) are said to exhibit *ideal behavior* or to approximate the traits of an **ideal gas**. An ideal gas is a hypothetical construct that may be used along with *kinetic molecular theory* to effectively explain the gas laws as will be described in a later module of this chapter. Although all the calculations presented in this module assume ideal behavior, this assumption is only reasonable for gases under conditions of relatively low pressure and high temperature. In the final module of this chapter, a modified gas law will be introduced that accounts for the *non-ideal* behavior observed for many gases at relatively high pressures and low temperatures.

The ideal gas equation contains five terms, the gas constant R and the variable properties P, V, n, and T. Specifying any four of these terms will permit use of the ideal gas law to calculate the fifth term as demonstrated in the following example exercises.

✓ Example 2.1.1.5: Using the Ideal Gas Law

Methane, CH_4, is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of CH_4. What is the volume of this much methane at 25 °C and 745 torr?

Solution

We must rearrange $PV = nRT$ to solve for V:

$$V = \frac{nRT}{P}$$

If we choose to use R = 0.08206 L atm mol^{-1} K^{-1}, then the amount must be in moles, temperature must be in kelvin, and pressure must be in atm.

Converting into the "right" units:

$$n = 655 \ \text{g} \ \cancel{\text{CH}_4} \times \frac{1 \text{ mol}}{16.043 \text{ g } \cancel{\text{CH}_4}} = 40.8 \text{ mol}$$

$$T = 25^{\circ}C + 273 = 298 \text{ K}$$

$$P = 745 \text{ torr } \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.980 \text{ atm}$$

$$V = \frac{nRT}{P} = \frac{(40.8 \ \cancel{\text{mol}}) \left(0.08206 \ L \ \text{ atm} \ \cancel{\text{mol}^{-1} \text{K}^{-1}}\right) (298 \ \ \cancel{\text{K}})}{0.980 \ \ \cancel{\text{atm}}} = 1.02 \times 10^3 \text{ L}$$

It would require 1020 L (269 gal) of gaseous methane at about 1 atm of pressure to replace 1 gal of gasoline. It requires a large container to hold enough methane at 1 atm to replace several gallons of gasoline.

? Exercise 2.1.1.5

Calculate the pressure in bar of 2520 moles of hydrogen gas stored at 27 °C in the 180-L storage tank of a modern hydrogen-powered car.

Answer

350 bar

If the number of moles of an ideal gas are kept constant under two different sets of conditions, a useful mathematical relationship called the **combined gas law** is obtained:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

using units of atm, L, and K. Both sets of conditions are equal to the product of n R (where n = the number of moles of the gas and R is the ideal gas law constant).

✓ Example 2.1.1.6: Using the Combined Gas Law

When filled with air, a typical scuba tank with a volume of 13.2 L has a pressure of 153 atm (Figure 2.1.1.7). If the water temperature is 27 °C, how many liters of air will such a tank provide to a diver's lungs at a depth of approximately 70 feet in the ocean where the pressure is 3.13 atm?

Figure 2.1.1.7: Scuba divers use compressed air to breathe while underwater. (credit: modification of work by Mark Goodchild)

Letting *1* represent the air in the scuba tank and *2* represent the air in the lungs, and noting that body temperature (the temperature the air will be in the lungs) is 37 °C, we have:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \rightarrow \frac{(153 atm)(13.2 L)}{(300 K)} = \frac{(3.13 atm)\,(V_2)}{(310 K)}$$

Solving for V_2:

$$V_2 = \frac{(153 \text{ atm })(13.2 L)(310 K)}{(300 K)(3.13 \text{ atm })} = 667 L$$

(Note: Be advised that this particular example is one in which the assumption of ideal gas behavior is not very reasonable, since it involves gases at relatively high pressures and low temperatures. Despite this limitation, the calculated volume can be viewed as a good “ballpark” estimate.)

Exercise 2.1.1.6

A sample of ammonia is found to occupy 0.250 L under laboratory conditions of 27 °C and 0.850 atm. Find the volume of this sample at 0 °C and 1.00 atm.

Answer

0.193 L

Chemistry in Everyday Life: The Interdependence between Ocean Depth and Pressure in Scuba Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in Figure 2.1.1.8) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.

Figure $2.1.1.8$: Scuba divers, whether at the Great Barrier Reef or in the Caribbean, must be aware of buoyancy, pressure equalization, and the amount of time they spend underwater, to avoid the risks associated with pressurized gases in the body. (credit: Kyle Taylor)

Pressure increases with ocean depth, and the pressure changes most rapidly as divers reach the surface. The pressure a diver experiences is the sum of all pressures above the diver (from the water and the air). Most pressure measurements are given in units of atmospheres, expressed as “atmospheres absolute” or ATA in the diving community: Every 33 feet of salt water represents 1 ATA of pressure in addition to 1 ATA of pressure from the atmosphere at sea level. As a diver descends, the increase in pressure causes the body’s air pockets in the ears and lungs to compress; on the ascent, the decrease in pressure causes these air pockets to expand, potentially rupturing eardrums or bursting the lungs. Divers must therefore undergo equalization by adding air to body airspaces on the descent by breathing normally and adding air to the mask by breathing out of the nose or adding air to the ears and sinuses by equalization techniques; the corollary is also true on ascent, divers must release air from the body to maintain equalization. Buoyancy, or the ability to control whether a diver sinks or floats, is controlled by the buoyancy compensator (BCD). If a diver is ascending, the air in their BCD expands because of lower pressure according to Boyle’s law (decreasing the pressure of gases increases the volume). The expanding air increases the buoyancy of the diver, and they begin to ascend. The diver must vent air from the BCD or risk an uncontrolled ascent that could rupture the lungs. In descending, the increased pressure causes the air in the BCD to compress and the diver sinks much more quickly; the diver must add air to the BCD or risk an uncontrolled descent, facing much higher pressures near the ocean floor. The pressure also impacts how long a diver can stay underwater before ascending. The deeper a diver dives, the more compressed the air that is breathed because of increased pressure: If a diver dives 33 feet, the pressure is 2 ATA and the air would be compressed to one-half of its original volume. The diver uses up available air twice as fast as at the surface.

Standard Conditions of Temperature and Pressure

We have seen that the volume of a given quantity of gas and the number of molecules (moles) in a given volume of gas vary with changes in pressure and temperature. Chemists sometimes make comparisons against a **standard temperature and pressure (STP)** for reporting properties of gases: 273.15 K and 1 atm (101.325 kPa).[1] At STP, one mole of an ideal gas has a volume of about 22.4 L—this is referred to as the **standard molar volume** (Figure $2.1.1.9$).

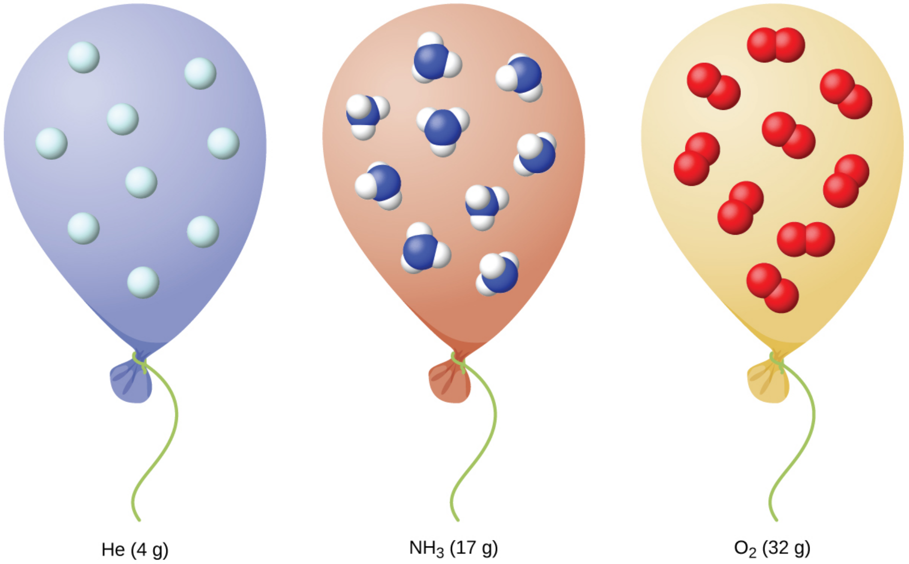


Figure 2.1.1.9: Regardless of its chemical identity, one mole of gas behaving ideally occupies a volume of ~22.4 L at STP.

Footnotes

- 1The IUPAC definition of standard pressure was changed from 1 atm to 1 bar (100 kPa) in 1982, but the prior definition remains in use by many literature resources and will be used in this text.

2.1.2: Stoichiometry of Gaseous Substances, Mixtures, and Reactions

Learning Objectives

By the end of this section, you will be able to:

- Use the ideal gas law to compute gas densities and molar masses
- Perform stoichiometric calculations involving gaseous substances
- State Dalton's law of partial pressures and use it in calculations involving gaseous mixtures

The study of the chemical behavior of gases was part of the basis of perhaps the most fundamental chemical revolution in history. French nobleman Antoine Lavoisier, widely regarded as the "father of modern chemistry," changed chemistry from a qualitative to a quantitative science through his work with gases. He discovered the law of conservation of matter, discovered the role of oxygen in combustion reactions, determined the composition of air, explained respiration in terms of chemical reactions, and more. He was a casualty of the French Revolution, guillotined in 1794. Of his death, mathematician and astronomer Joseph-Louis Lagrange said, "It took the mob only a moment to remove his head; a century will not suffice to reproduce it."[2] Much of the knowledge we do have about Lavoisier's contributions is due to his wife, Marie-Anne Paulze Lavoisier, who worked with him in his lab. A trained artist fluent in several languages, she created detailed illustrations of the equipment in his lab, and translated texts from foreign scientists to complement his knowledge. After his execution, she was instrumental in publishing Lavoisier's major treatise, which unified many concepts of chemistry and laid the groundwork for significant further study.

As described in an earlier chapter of this text, we can turn to chemical stoichiometry for answers to many of the questions that ask "How much?" The essential property involved in such use of stoichiometry is the amount of substance, typically measured in moles (*n*). For gases, molar amount can be derived from convenient experimental measurements of pressure, temperature, and volume. Therefore, these measurements are useful in assessing the stoichiometry of pure gases, gas mixtures, and chemical reactions involving gases. This section will not introduce any new material or ideas, but will provide examples of applications and ways to integrate concepts already discussed.

Gas Density and Molar Mass

The ideal gas law described previously in this chapter relates the properties of pressure P, volume V, temperature T, and molar amount n. This law is universal, relating these properties in identical fashion regardless of the chemical identity of the gas:

$$PV = nRT$$

The density d of a gas, on the other hand, is determined by its identity. As described in another chapter of this text, the density of a substance is a characteristic property that may be used to identify the substance.

$$d = \frac{m}{V}$$

Rearranging the ideal gas equation to isolate V and substituting into the density equation yields

$$d = \frac{mP}{nRT} = \left(\frac{m}{n}\right)\frac{P}{RT}$$

The ratio m/n is the definition of molar mass, $\mathcal{M}$:

$$\mathcal{M} = \frac{m}{n}$$

The density equation can then be written

$$d = \frac{\mathcal{M}P}{RT}$$

This relation may be used for calculating the densities of gases of known identities at specified values of pressure and temperature as demonstrated in Example 2.1.2.1

✓ Example 2.1.2.1: Measuring Gas Density

What is the density of molecular nitrogen gas at STP?

Solution

The molar mass of molecular nitrogen, N_2, is 28.01 g/mol. Substituting this value along with standard temperature and pressure into the gas density equation yields

$$d = \frac{\mathscr{M}P}{RT} = \frac{(28.01\ \mathrm{g/mol})(1.00\ \mathrm{atm})}{\left(0.0821\ \mathrm{L \cdot atm \cdot mol^{-1} K^{-1}}\right)(273\ \mathrm{K})} = 1.25\ \mathrm{g}\ /\ \mathrm{L}$$

? Exercise 2.1.2.1

What is the density of molecular hydrogen gas at 17.0 °C and a pressure of 760 torr?

Answer

d = 0.0847 g/L

When the identity of a gas is unknown, measurements of the mass, pressure, volume, and temperature of a sample can be used to calculate the molar mass of the gas (a useful property for identification purposes). Combining the ideal gas equation

$$PV = nRT$$

and the definition of molar mass

$$\mathscr{M} = \frac{m}{n}$$

yields the following equation:

$$\mathscr{M} = \frac{mRT}{PV}$$

Determining the molar mass of a gas via this approach is demonstrated in Example 2.1.2.2

✓ Example 2.1.2.2: Determining the Molecular Formula of a Gas from its Molar Mass and Empirical Formula

Cyclopropane, a gas once used with oxygen as a general anesthetic, is composed of 85.7% carbon and 14.3% hydrogen by mass. Find the empirical formula. If 1.56 g of cyclopropane occupies a volume of 1.00 L at 0.984 atm and 50 °C, what is the molecular formula for cyclopropane?

Solution

First determine the empirical formula of the gas. Assume 100 g and convert the percentage of each element into grams. Determine the number of moles of carbon and hydrogen in the 100-g sample of cyclopropane. Divide by the smallest number of moles to relate the number of moles of carbon to the number of moles of hydrogen.

$$85.7\ \mathrm{g}\ C \times \frac{1\ \mathrm{mol}\ C}{12.01\ \mathrm{g}\ C} = 7.136\ \mathrm{mol}\ C$$

$$14.3\ \mathrm{g}\ H \times \frac{1\ \mathrm{mol}\ H}{1.01\ \mathrm{g}\ H} = 14.158\ \mathrm{mol}\ H$$

In the last step, realize that the smallest whole number ratio is the empirical formula:

$$\frac{7.136}{7.136} = 1.00\ \mathrm{mol}\ C$$

$$\frac{14.158}{7.136} = 1.98\ \mathrm{mol}\ H$$

Empirical formula is $\mathrm{CH_2}$ [empirical mass (EM) of 14.03 g/empirical unit].

Next, use the provided values for mass, pressure, temperature and volume to compute the molar mass of the gas:

$$\mathscr{M} = \frac{mRT}{PV} = \frac{(1.56\ \text{g})\left(0.0821\ \text{L}\cdot\text{atm}\cdot\text{mol}^{-1}\text{K}^{-1}\right)(323\ \text{K})}{(0.984\ \text{atm})(1.00\ \text{L})} = 42.0\ \text{g}/\text{mol}$$

Comparing the molar mass to the empirical formula mass shows how many empirical formula units make up a molecule:

$$\frac{\mathscr{M}}{EM} = \frac{42.0\ \text{g}/\text{mol}}{14.0\ \text{g}/\text{mol}} = 3$$

The molecular formula is thus derived from the empirical formula by multiplying each of its subscripts by three:

$$(\text{CH}_2)_3 = \text{C}_3\text{H}_6$$

? Exercise 2.1.2.2

Acetylene, a fuel used welding torches, is composed of 92.3% C and 7.7% H by mass. Find the empirical formula. If 1.10 g of acetylene occupies of volume of 1.00 L at 1.15 atm and 59.5 °C, what is the molecular formula for acetylene?

Answer

Empirical formula, CH; Molecular formula, C_2H_2

✓ Example 2.1.2.3: Determining the Molar Mass of a Volatile Liquid

The approximate molar mass of a volatile liquid can be determined by:

1. Heating a sample of the liquid in a flask with a tiny hole at the top, which converts the liquid into gas that may escape through the hole
2. Removing the flask from heat at the instant when the last bit of liquid becomes gas, at which time the flask will be filled with only gaseous sample at ambient pressure
3. Sealing the flask and permitting the gaseous sample to condense to liquid, and then weighing the flask to determine the sample's mass (see Figure 2.1.2.1)

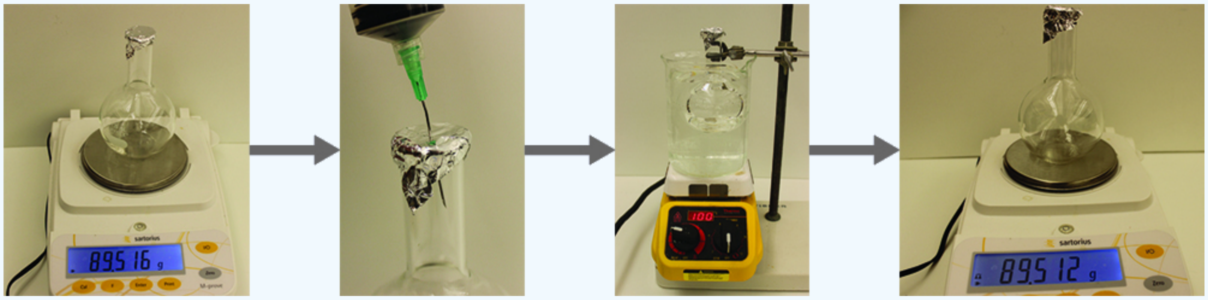


Figure 2.1.2.1: When the volatile liquid in the flask is heated past its boiling point, it becomes gas and drives air out of the flask. At the flask is filled with volatile liquid gas at the same pressure as the atmosphere. If the flask is then cooled to room temperature, the gas condenses and the mass of the gas that filled the flask, and is now liquid, can be measured. (credit: modification of work by Mark Ott)

Using this procedure, a sample of chloroform gas weighing 0.494 g is collected in a flask with a volume of 129 cm^3 at 99.6 °C when the atmospheric pressure is 742.1 mm Hg. What is the approximate molar mass of chloroform?

Solution

Since $\mathscr{M} = \frac{m}{n}$ and $n = \frac{PV}{RT}$ substituting and rearranging gives $\mathscr{M} = \frac{mRT}{PV}$,

then

$$\mathscr{M} = \frac{mRT}{PV} = \frac{(0.494\ \text{g}) \times 0.08206\ \text{L}\cdot\text{atm}/\text{mol K} \ \times 372.8\ \text{K}}{0.976\ \text{atm} \times 0.129\ \text{L}} = 120\ \text{g}/\text{mol}$$

? Exercise 2.1.2.3

A sample of phosphorus that weighs 3.243×10^{-2} g exerts a pressure of 31.89 kPa in a 56.0-mL bulb at 550 °C. What are the molar mass and molecular formula of phosphorus vapor?

Answer

124 g/mol P_4

The Pressure of a Mixture of Gases: Dalton's Law

Unless they chemically react with each other, the individual gases in a mixture of gases do not affect each other's pressure. Each individual gas in a mixture exerts the same pressure that it would exert if it were present alone in the container (Figure 2.1.2.2). The pressure exerted by each individual gas in a mixture is called its **partial pressure**. This observation is summarized by **Dalton's law of partial pressures**: *The total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases*:

$$P_{\text{Total}} = P_A + P_B + P_C + \ldots = \sum_i P_i$$

In the equation P_{Total} is the total pressure of a mixture of gases, P_A is the partial pressure of gas A; P_B is the partial pressure of gas B; P_C is the partial pressure of gas C; and so on.

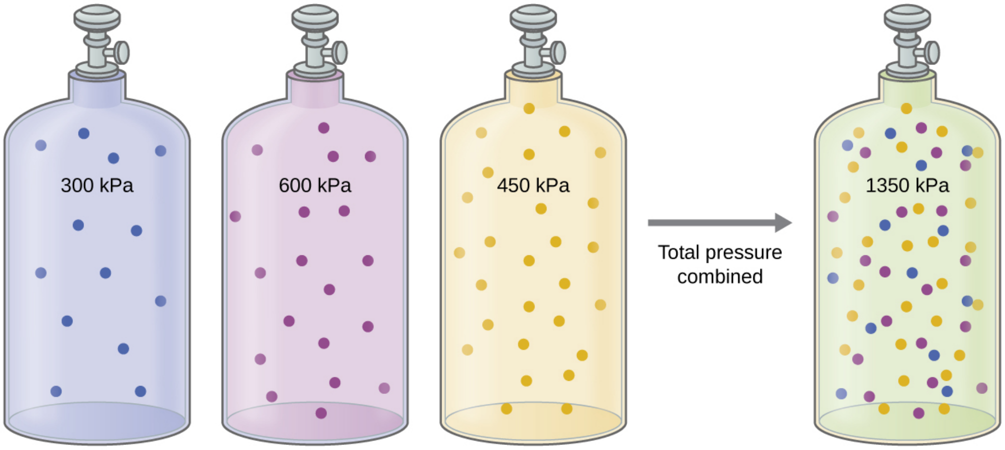


Figure 2.1.2.2: If equal-volume cylinders containing gasses at pressures of 300 kPa, 450 kPa, and 600 kPa are all combined in the same-size cylinder, the total pressure of the gas mixture is 1350 kPa.

The partial pressure of gas A is related to the total pressure of the gas mixture via its **mole fraction** (X), a unit of concentration defined as the number of moles of a component of a solution divided by the total number of moles of all components:

$$P_A = X_A \times P_{\text{Total}}$$

where

$$X_A = \frac{n_A}{n_{\text{Total}}}$$

where P_A, X_A, and n_A are the partial pressure, mole fraction, and number of moles of gas A, respectively, and n_{Total} is the number of moles of all components in the mixture.

✓ Example 2.1.2.4: The Pressure of a Mixture of Gases

A 10.0-L vessel contains 2.50 10^{-3} mol of H_2, 1.00 10^{-3} mol of He, and 3.00 10^{-4} mol of Ne at 35 °C.

a. What are the partial pressures of each of the gases?
b. What is the total pressure in atmospheres?

Solution

The gases behave independently, so the partial pressure of each gas can be determined from the ideal gas equation, using $P = \frac{nRT}{V}$:

$$\begin{aligned} P_{H_2} &= \frac{\left(2.50 \times 10^{-3} \ \cancel{\text{mol}}\right)\left(0.08206 \ \cancel{\text{L}}\,\text{atm} \ \text{mol}^{-1} \cancel{\text{K}^{-1}}\right)\left(308 \ \cancel{\text{K}}\right)}{10.0 \ \cancel{\text{L}}} = 6.32 \times 10^{-3} \text{ atm} \\ &= \frac{\left(1.00 \times 10^{-3} \ \cancel{\text{mol}}\right)\left(0.08206 \ \cancel{\text{L}}\,\text{atm} \ \text{mol}^{-1} \cancel{\text{K}^{-1}}\right)\left(308 \ \cancel{\text{K}}\right)}{10.0 \ \cancel{\text{L}}} = 2.53 \times 10^{-3} \text{ atm} \\ &= \frac{\left(3.00 \times 10^{-4} \ \cancel{\text{mol}}\right)\left(0.08206 \ \cancel{\text{L}}\,\text{atm} \ \text{mol}^{-1} \cancel{\text{K}^{-1}}\right)\left(308 \ \cancel{\text{K}}\right)}{10.0 \ \cancel{\text{L}}} = 7.58 \times 10^{-4} \text{ atm} \end{aligned}$$

The total pressure is given by the sum of the partial pressures:

$$P_T = P_{H_2} + P_{He} + P_{Ne} = (0.00632 + 0.00253 + 0.00076) \text{ atm} = 9.61 \times 10^{-3} \text{ atm}$$

? Exercise 2.1.2.4

A 5.73-L flask at 25 °C contains 0.0388 mol of N_2, 0.147 mol of CO, and 0.0803 mol of H_2. What is the total pressure in the flask in atmospheres?

Answer

1.137 atm

Here is another example of this concept, but dealing with mole fraction calculations.

✓ Example 2.1.2.5: The Pressure of a Mixture of Gases

A gas mixture used for anesthesia contains 2.83 mol oxygen, O_2, and 8.41 mol nitrous oxide, N_2O. The total pressure of the mixture is 192 kPa.

a. What are the mole fractions of O_2 and N_2O?
b. What are the partial pressures of O_2 and N_2O?

Solution

The mole fraction is given by $X_A = \frac{n_A}{n_{\text{Total}}}$ and the partial pressure is $P_A = X_A P_{Total}$.

For O_2,

$$X_{O_2} = \frac{n_{O_2}}{n_{\text{Total}}} = \frac{2.83 mol}{(2.83 + 8.41) mol} = 0.252$$

and $P_{O_2} = X_{O_2} \times P_{\text{Total}} = 0.252 \times 192 kPa = 48.4 kPa$

For N_2O,

$$X_{N_2O} = \frac{n_{N_2O}}{n_{\text{Total}}} = \frac{8.41 mol}{(2.83 + 8.41) mol} = 0.748$$

and

$$P_{N_2O} = X_{N_2O} \times P_{\text{Total}} = 0.748 \times 192 kPa = 144 kPa$$

? Exercise 2.1.2.5

What is the pressure of a mixture of 0.200 g of H_2, 1.00 g of N_2, and 0.820 g of Ar in a container with a volume of 2.00 L at 20 °C?

Answer

1.87 atm

Collection of Gases over Water

A simple way to collect gases that do not react with water is to capture them in a bottle that has been filled with water and inverted into a dish filled with water. The pressure of the gas inside the bottle can be made equal to the air pressure outside by raising or lowering the bottle. When the water level is the same both inside and outside the bottle (Figure 2.1.2.3), the pressure of the gas is equal to the atmospheric pressure, which can be measured with a barometer.

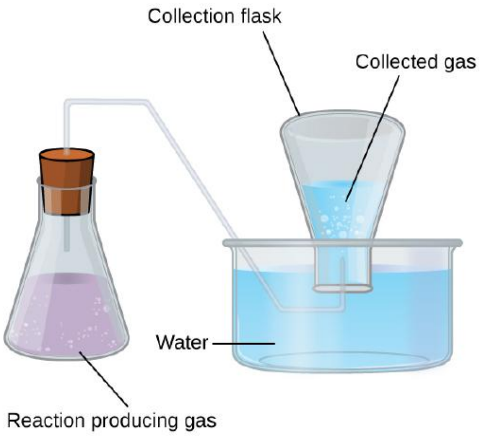


Figure 2.1.2.3: When a reaction produces a gas that is collected above water, the trapped gas is a mixture of the gas produced by the reaction and water vapor. If the collection flask is appropriately positioned to equalize the water levels both within and outside the flask, the pressure of the trapped gas mixture will equal the atmospheric pressure outside the flask (see the earlier discussion of manometers).

However, there is another factor we must consider when we measure the pressure of the gas by this method. Water evaporates and there is always gaseous water (water vapor) above a sample of liquid water. As a gas is collected over water, it becomes saturated with water vapor and the total pressure of the mixture equals the partial pressure of the gas plus the partial pressure of the water vapor. The pressure of the pure gas is therefore equal to the total pressure minus the pressure of the water vapor—this is referred to as the "dry" gas pressure, that is, the pressure of the gas only, without water vapor. The **vapor pressure of water**, which is the pressure exerted by water vapor in equilibrium with liquid water in a closed container, depends on the temperature (Figure 2.1.2.4); more detailed information on the temperature dependence of water vapor can be found in Table 2.1.2.1, and vapor pressure will be discussed in more detail in the next chapter on liquids.

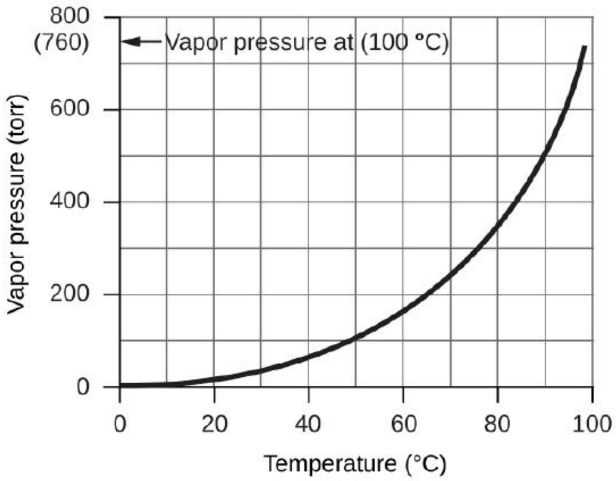


Figure 2.1.2.4: This graph shows the vapor pressure of water at sea level as a function of temperature.

Table 2.1.2.1: Vapor Pressure of Ice and Water in Various Temperatures at Sea Level

Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (torr)
–10	1.95	18	15.5	30	31.8
–5	3.0	19	16.5	35	42.2
–2	3.9	20	17.5	40	55.3
0	4.6	21	18.7	50	92.5
2	5.3	22	19.8	60	149.4
4	6.1	23	21.1	70	233.7
6	7.0	24	22.4	80	355.1
8	8.0	25	23.8	90	525.8
10	9.2	26	25.2	95	633.9
12	10.5	27	26.7	99	733.2
14	12.0	28	28.3	100.0	760.0
16	13.6	29	30.0	101.0	787.6

✓ Example 2.1.2.6: Pressure of a Gas Collected Over Water

If 0.200 L of argon is collected over water at a temperature of 26 °C and a pressure of 750 torr in a system like that shown in Figure 2.1.2.3, what is the partial pressure of argon?

Solution

According to Dalton’s law, the total pressure in the bottle (750 torr) is the sum of the partial pressure of argon and the partial pressure of gaseous water:

$$P_T = P_{Ar} + P_{H_2O}$$

Rearranging this equation to solve for the pressure of argon gives:

$$P_{Ar} = P_T - P_{H_2O}$$

The pressure of water vapor above a sample of liquid water at 26 °C is 25.2 torr (Appendix E), so:

$$P_{Ar} = 750 \text{ torr } - 25.2 \text{ torr } = 725 \text{ torr}$$

Exercise 2.1.2.6

A sample of oxygen collected over water at a temperature of 29.0 °C and a pressure of 764 torr has a volume of 0.560 L. What volume would the dry oxygen from this sample have under the same conditions of temperature and pressure?

Answer

0.537 L

Chemical Stoichiometry and Gases

Chemical stoichiometry describes the quantitative relationships between reactants and products in chemical reactions.

We have previously measured quantities of reactants and products using masses for solids and volumes in conjunction with the molarity for solutions; now we can also use gas volumes to indicate quantities. If we know the volume, pressure, and temperature of a gas, we can use the ideal gas equation to calculate how many moles of the gas are present. If we know how many moles of a gas are involved, we can calculate the volume of a gas at any temperature and pressure.

Avogadro's Law Revisited

Sometimes we can take advantage of a simplifying feature of the stoichiometry of gases that solids and solutions do not exhibit: All gases that show ideal behavior contain the same number of molecules in the same volume (at the same temperature and pressure). Thus, the ratios of volumes of gases involved in a chemical reaction are given by the coefficients in the equation for the reaction, provided that the gas volumes are measured at the same temperature and pressure.

We can extend Avogadro's law (that the volume of a gas is directly proportional to the number of moles of the gas) to chemical reactions with gases: Gases combine, or react, in definite and simple proportions by volume, provided that all gas volumes are measured at the same temperature and pressure. For example, since nitrogen and hydrogen gases react to produce ammonia gas according to

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

a given volume of nitrogen gas reacts with three times that volume of hydrogen gas to produce two times that volume of ammonia gas, if pressure and temperature remain constant.

The explanation for this is illustrated in Figure 2.1.2.5. According to Avogadro's law, equal volumes of gaseous N_2, H_2, and NH_3, at the same temperature and pressure, contain the same number of molecules. Because one molecule of N_2 reacts with three molecules of H_2 to produce two molecules of NH_3, the volume of H_2 required is three times the volume of N_2, and the volume of NH_3 produced is two times the volume of N_2.

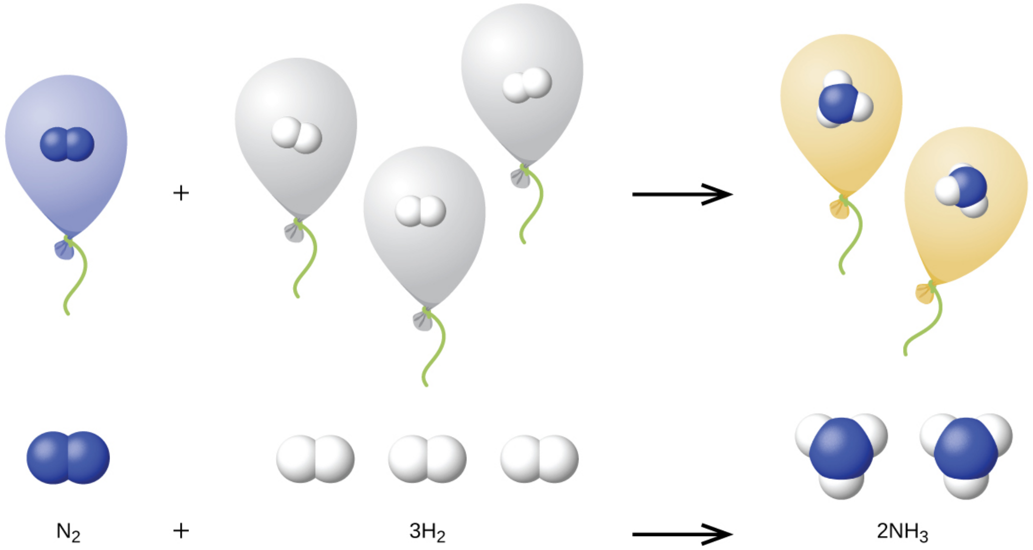


Figure 2.1.2.5: One volume of N_2 combines with three volumes of H_2 to form two volumes of NH_3.

✓ Example 2.1.2.7: Reaction of Gases

Propane, $C_3H_8(g)$, is used in gas grills to provide the heat for cooking. What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 2.7 L of propane measured under the same conditions of temperature and pressure? Assume that the propane undergoes complete combustion.

Solution

The ratio of the volumes of C_3H_8 and O_2 will be equal to the ratio of their coefficients in the balanced equation for the reaction:

$$\underbrace{1 \text{ volume} + 5 \text{ volumes}}_{C_3H_8(g)+5\,O_2(g)} \longrightarrow \underbrace{3 \text{ volumes} + 4 \text{ volumes}}_{3\,CO_2(g)+4\,H_2O(l)}$$

From the equation, we see that one volume of C_3H_8 will react with five volumes of O_2:

$$2.7\ \cancel{L}\ C_3H_8 \times \frac{5\text{ L } O_2}{1\ \ L\cancel{C_3H_8}} = 13.5\text{ L } O_2$$

A volume of 13.5 L of O_2 will be required to react with 2.7 L of C_3H_8.

? Exercise 2.1.2.7

An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas, C_2H_2, at 0 °C and 1 atm. How many tanks of oxygen, each providing $7.00\ 10^3$ L of O_2 at 0 °C and 1 atm, will be required to burn the acetylene?

$$2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$$

Answer

3.34 tanks ($2.34\ 10^4$ L)

✓ Example 2.1.2.8: Volumes of Reacting Gases

Ammonia is an important fertilizer and industrial chemical. Suppose that a volume of 683 billion cubic feet of gaseous ammonia, measured at 25 °C and 1 atm, was manufactured. What volume of $H_2(g)$, measured under the same conditions, was required to prepare this amount of ammonia by reaction with N_2?

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

Solution

Because equal volumes of H_2 and NH_3 contain equal numbers of molecules and each three molecules of H_2 that react produce two molecules of NH_3, the ratio of the volumes of H_2 and NH_3 will be equal to 3:2. Two volumes of NH_3, in this case in units of billion ft^3, will be formed from three volumes of H_2:

$$683 \text{ billion } ft^3\, NH_3 \times \frac{3 \text{ billion } ft^3\, H_2}{2 \text{ billion } ft^3\, NH_3} = 1.02 \times 10^3 \text{ billion } ft^3\, H_2$$

The manufacture of 683 billion ft^3 of NH_3 required 1020 billion ft^3 of H_2. (At 25 °C and 1 atm, this is the volume of a cube with an edge length of approximately 1.9 miles.)

? Exercise 2.1.2.8

What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 17.0 L of ethylene, $C_2H_4(g)$, measured under the same conditions of temperature and pressure? The products are CO_2 and water vapor.

Answer

51.0 L

✓ Example 2.1.2.9: Volume of Gaseous Product

What volume of hydrogen at 27 °C and 723 torr may be prepared by the reaction of 8.88 g of gallium with an excess of hydrochloric acid?

$$2\,\text{Ga}(s) + 6\,\text{HCl}(aq) \longrightarrow 2\,\text{GaCl}_3(aq) + 3\,\text{H}_2(g)$$

Solution

Convert the provided mass of the limiting reactant, Ga, to moles of hydrogen produced:

$$8.88\ \text{g}\ \cancel{\text{Ga}} \times \frac{1\ \text{mol}\ \cancel{\text{Ga}}}{69.723\ \text{g}\ \cancel{\text{Ga}}} \times \frac{3\ \text{mol H}_2}{2\ \text{mol}\ \cancel{\text{Ga}}} = 0.191\ \text{mol H}_2$$

Convert the provided temperature and pressure values to appropriate units (K and atm, respectively), and then use the molar amount of hydrogen gas and the ideal gas equation to calculate the volume of gas:

$$V = \left(\frac{nRT}{P}\right) = \frac{0.191\ \cancel{\text{mol}} \times 0.08206\ \text{L atm}\ \cancel{\text{mol}}^{-1}\,\text{K}^{-1} \times 300\ \text{K}}{0.951\ \cancel{\text{atm}}} = 4.94\ \text{L}$$

? Exercise 2.1.2.9

Sulfur dioxide is an intermediate in the preparation of sulfuric acid. What volume of SO_2 at 343 °C and 1.21 atm is produced by burning l.00 kg of sulfur in excess oxygen?

Answer

1.30 10^3 L

How Sciences Interconnect: Greenhouse Gases and Climate Change

The thin skin of our atmosphere keeps the earth from being an ice planet and makes it habitable. In fact, this is due to less than 0.5% of the air molecules. Of the energy from the sun that reaches the earth, almost $\frac{1}{3}$ is reflected back into space, with the rest absorbed by the atmosphere and the surface of the earth. Some of the energy that the earth absorbs is re-emitted as infrared (IR) radiation, a portion of which passes back out through the atmosphere into space. Most if this IR radiation, however, is absorbed by certain atmospheric gases, effectively trapping heat within the atmosphere in a phenomenon known as the greenhouse effect. This effect maintains global temperatures within the range needed to sustain life on earth. Without our atmosphere, the earth's average temperature would be lower by more than 30 °C (nearly 60 °F). The major greenhouse gases (GHGs) are water vapor, carbon dioxide, methane, and ozone. Since the Industrial Revolution, human activity has been increasing the concentrations of GHGs, which have changed the energy balance and are significantly altering the earth’s climate (Figure 2.1.2.6).

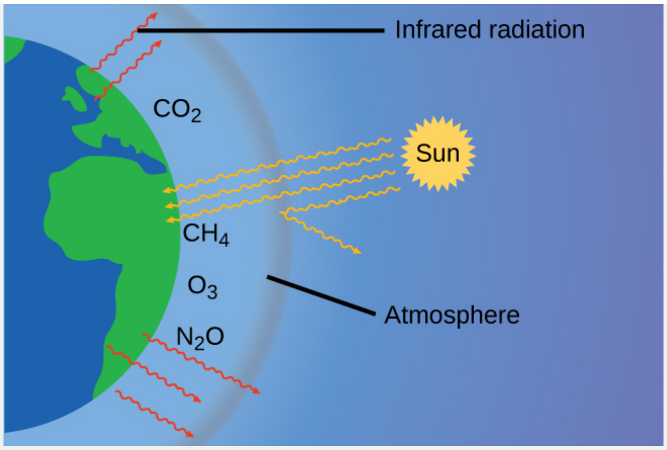


Figure 2.1.2.6: Greenhouse gases trap enough of the sun's energy to make the planet habitable—this is known as the greenhouse effect. Human activities are increasing greenhouse gas levels, warming the planet and causing more extreme weather events.

There is strong evidence from multiple sources that higher atmospheric levels of CO2 are caused by human activity, with fossil fuel burning accounting for about $\frac{3}{4}$ of the recent increase in CO2. Reliable data from ice cores reveals that CO2 concentration in the atmosphere is at the highest level in the past 800,000 years; other evidence indicates that it may be at its highest level in 20 million years. In recent years, the CO2 concentration has increased preindustrial levels of ~280 ppm to more than 400 ppm today (Figure 2.1.2.7).

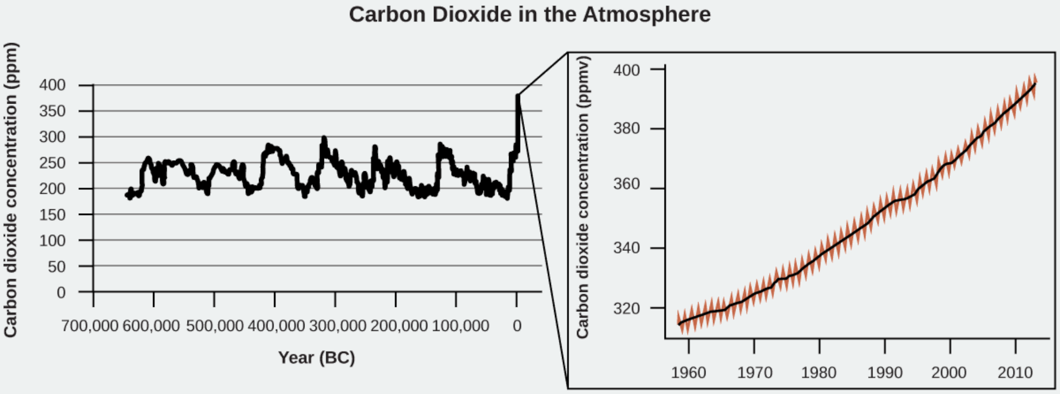


Figure 2.1.2.7: CO_2 levels over the past 700,000 years were typically from 200–300 ppm, with a steep, unprecedented increase over the past 50 years.

Link to Learning

Click here to see a 2-minute video explaining greenhouse gases and global warming.

Portrait of a Chemist: Susan Solomon

Atmospheric and climate scientist Susan Solomon (Figure 2.1.2.8) is the author of one of *The New York Times* books of the year (*The Coldest March*, 2001), one of Time magazine's 100 most influential people in the world (2008), and a working group leader of the Intergovernmental Panel on Climate Change (IPCC), which was the recipient of the 2007 Nobel Peace Prize. She helped determine and explain the cause of the formation of the ozone hole over Antarctica, and has authored many important papers on climate change. She has been awarded the top scientific honors in the US and France (the National Medal of Science and the Grande Medaille, respectively), and is a member of the National Academy of Sciences, the Royal Society, the French Academy of Sciences, and the European Academy of Sciences. Formerly a professor at the University of Colorado, she is now at MIT, and continues to work at NOAA.

Figure 2.1.2.8: Susan Solomon’s research focuses on climate change and has been instrumental in determining the cause of the ozone hole over Antarctica. (credit: National Oceanic and Atmospheric Administration)

For more information, watch this video about Susan Solomon.

Footnotes

- [2] “Quotations by Joseph-Louis Lagrange,” last modified February 2006, accessed February 10, 2015, www-history.mcs.st-andrews.ac.../Lagrange.html

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2.1.3: The Kinetic-Molecular Theory

Learning Objectives

- State the postulates of the kinetic-molecular theory
- Use this theory's postulates to explain the gas laws

The gas laws that we have seen to this point, as well as the ideal gas equation, are empirical, that is, they have been derived from experimental observations. The mathematical forms of these laws closely describe the macroscopic behavior of most gases at pressures less than about 1 or 2 atm. Although the gas laws describe relationships that have been verified by many experiments, they do not tell us why gases follow these relationships.

The **kinetic molecular theory** (KMT) is a simple microscopic model that effectively explains the gas laws described in previous modules of this chapter. This theory is based on the following five postulates described here. (Note: The term "molecule" will be used to refer to the individual chemical species that compose the gas, although some gases are composed of atomic species, for example, the noble gases.)

1. Gases are composed of molecules that are in continuous motion, travelling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
2. The molecules composing the gas are negligibly small compared to the distances between them.
3. The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
4. Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are *elastic* (do not involve a loss of energy).
5. The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

The test of the KMT and its postulates is its ability to explain and describe the behavior of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will first look at the individual gas laws (Boyle's, Charles's, Amontons's, Avogadro's, and Dalton's laws) conceptually to see how the KMT explains them. Then, we will more carefully consider the relationships between molecular masses, speeds, and kinetic energies with temperature, and explain Graham's law.

The Kinetic-Molecular Theory Explains the Behavior of Gases, Part I

Recalling that gas pressure is exerted by rapidly moving gas molecules and depends directly on the number of molecules hitting a unit area of the wall per unit of time, we see that the KMT conceptually explains the behavior of a gas as follows:

- *Amontons's law.* If the temperature is increased, the average speed and kinetic energy of the gas molecules increase. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container, therefore increasing the pressure (Figure $2.1.3.1$).
- *Charles's law.* If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances traveled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease the both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which balance the effect of increased collision forces due to the greater kinetic energy at the higher temperature.
- *Boyle's law.* If the gas volume volume of a given amount of gas at a given temperature is decreased (that is, if the gas is *compressed*), the molecules will be exposed to a decreased container wall area. Collisions with the container wall will therefore occur more frequently and the pressure exerted by the gas will increase (Figure $2.1.3.1$).
- *Avogadro's law.* At constant pressure and temperature, the frequency and force of molecule-wall collisions are constant. Under such conditions, increasing the number of gaseous molecules will require a proportional increase in the container volume in order to yield a decrease in the number of collisions per unit area to compensate for the increased frequency of collisions (Figure $2.1.3.1$).
- *Dalton's Law.* Because of the large distances between them, the molecules of one gas in a mixture bombard the container walls with the same frequency whether other gases are present or not, and the total pressure of a gas mixture equals the sum of the (partial) pressures of the individual gases.

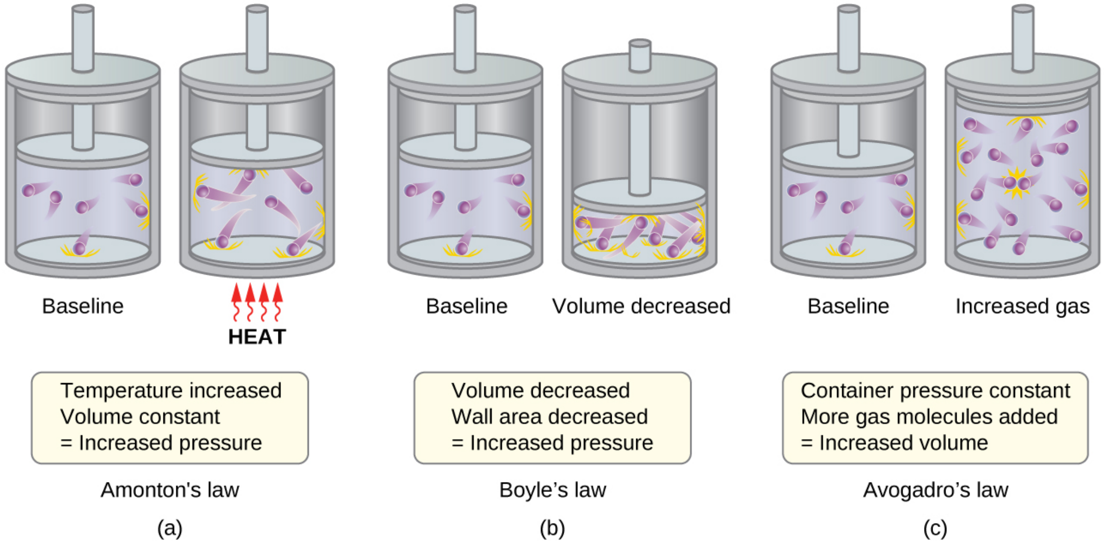


Figure 2.1.3.1: (a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time.

molecular speeds and Kinetic Energy

The previous discussion showed that the KMT qualitatively explains the behaviors described by the various gas laws. The postulates of this theory may be applied in a more quantitative fashion to derive these individual laws. To do this, we must first look at speeds and kinetic energies of gas molecules, and the temperature of a gas sample.

In a gas sample, individual molecules have widely varying speeds; however, because of the *vast* number of molecules and collisions involved, the molecular speed distribution and average speed are constant. This molecular speed distribution is known as a Maxwell-Boltzmann distribution, and it depicts the relative numbers of molecules in a bulk sample of gas that possesses a given speed (Figure 2.1.3.2).

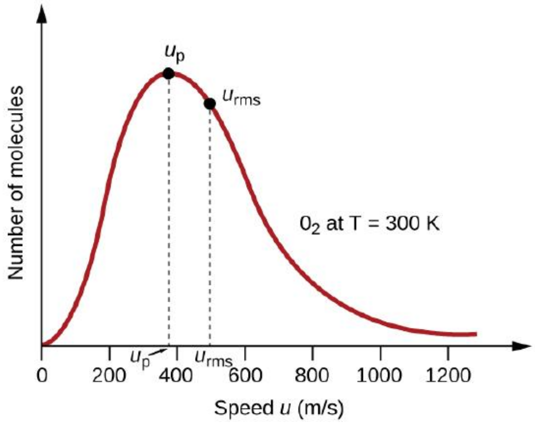


Figure 2.1.3.2: The molecular speed distribution for oxygen gas at 300 K is shown here. Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the most probable speed, v_p, is a little less than 400 m/s, while the root mean square speed, u_{rms}, is closer to 500 m/s.

The kinetic energy (KE) of a particle of mass (m) and speed (u) is given by:

$$KE = \frac{1}{2}mu^2$$

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules (J = kg m^2 s^{-2}). To deal with a large number of gas molecules, we use averages for both speed and kinetic energy. In the KMT, the root mean square speed of a particle, u_{rms}, is defined as the square root of the average of the squares of the speeds with n = the number of particles:

$$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \ldots}{n}}$$

The average kinetic energy for a mole of particles, KE_{avg}, is then equal to:

$$KE_{avg} = \frac{1}{2} M u_{rms}^2$$

where M is the molar mass expressed in units of kg/mol. The KE_{avg} of a mole of gas molecules is also directly proportional to the temperature of the gas and may be described by the equation:

$$KE_{avg} = \frac{3}{2} RT$$

where R is the gas constant and T is the kelvin temperature. When used in this equation, the appropriate form of the gas constant is 8.314 J/mol⋅K (8.314 kg $m^2s^{-2}mol^{-1}K^{-1}$). These two separate equations for KE_{avg} may be combined and rearranged to yield a relation between molecular speed and temperature:

$$\frac{1}{2} M u_{rms}^2 = \frac{3}{2} RT$$

with

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

Example 2.1.3.1: Calculation of u_{rms}

Calculate the root-mean-square speed for a nitrogen molecule at 30 °C.

Solution

Convert the temperature into Kelvin:

$$30^\circ C + 273 = 303 K$$

Determine the molar mass of nitrogen in kilograms:

`\frac{28.0 ~ \cancel{\text{g}}} }{1 ~\text{mol} } \times \frac{1~\text{kg} }{1000 ~ \cancel{\text{g}}}=0.028~ \text{kg/mol} \nonumber`

Replace the variables and constants in the root-mean-square speed equation, replacing Joules with the equivalent kg m^2s^{-2}:

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

$$u_{rms} = \sqrt{\frac{3(8.314 J/mol K)(303 K)}{(0.028 kg/mol)}} = \sqrt{2.70 \times 10^5 m^2 s^{-2}} = 519 m/s$$

Exercise 2.1.3.1

Calculate the root-mean-square speed for a mole of oxygen molecules at –23 °C.

Answer

441 m/s

If the temperature of a gas increases, its KE_{avg} increases, more molecules have higher speeds and fewer molecules have lower speeds, and the distribution shifts toward higher speeds overall, that is, to the right. If temperature decreases, KE_{avg} decreases, more molecules have lower speeds and fewer molecules have higher speeds, and the distribution shifts toward lower speeds overall, that is, to the left. This behavior is illustrated for nitrogen gas in Figure 2.1.3.3

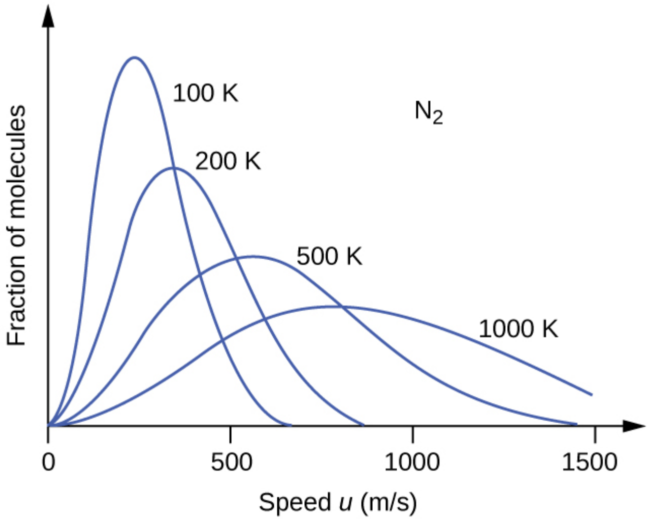


Figure 2.1.3.3: The molecular speed distribution for nitrogen gas (N_2) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases.

At a given temperature, all gases have the same KE_{avg} for their molecules. Gases composed of lighter molecules have more high-speed particles and a higher u_{rms}, with a speed distribution that peaks at relatively higher speeds. Gases consisting of heavier molecules have more low-speed particles, a lower u_{rms}, and a speed distribution that peaks at relatively lower speeds. This trend is demonstrated by the data for a series of noble gases shown in Figure 2.1.3.4

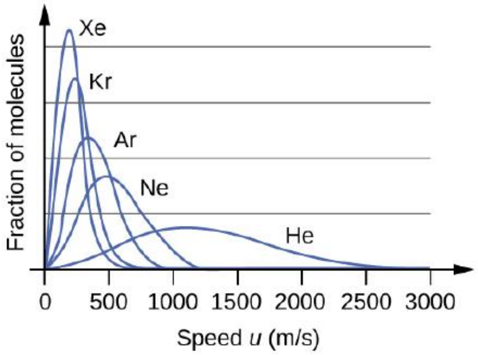


Figure 2.1.3.4: molecular speed is directly related to molecular mass. At a given temperature, lighter molecules move faster on average than heavier molecules.

Link to Learning

The gas simulator may be used to examine the effect of temperature on molecular speeds. Examine the simulator's "energy histograms" (molecular speed distributions) and "species information" (which gives average speed values) for molecules of different masses at various temperatures.

The Kinetic-Molecular Theory Explains the Behavior of Gases, Part II

According to Graham's law, the molecules of a gas are in rapid motion and the molecules themselves are small. The average distance between the molecules of a gas is large compared to the size of the molecules. As a consequence, gas molecules can move past each other easily and diffuse at relatively fast rates.

The rate of effusion of a gas depends directly on the (average) speed of its molecules:

$$\text{effusion rate } \propto u_{\text{rms}}$$

Using this relation, and the equation relating molecular speed to mass, Graham's law may be easily derived as shown here:

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

$$M = \frac{3RT}{u_{rms}^2} = \frac{3RT}{\bar{u}^2}$$

$$\frac{\text{effusion rate } A}{\text{effusion rate } B} = \frac{u_{rmsA}}{u_{rmsB}} = \frac{\sqrt{\frac{3RT}{M_A}}}{\sqrt{\frac{3RT}{M_B}}} = \sqrt{\frac{M_B}{M_A}}$$

The ratio of the rates of effusion is thus derived to be inversely proportional to the ratio of the square roots of their masses. This is the same relation observed experimentally and expressed as Graham’s law.

2.1.4: Non-Ideal Gas Behavior

Learning Objectives

By the end of this section, you will be able to:

- Describe the physical factors that lead to deviations from ideal gas behavior
- Explain how these factors are represented in the van der Waals equation
- Define compressibility (Z) and describe how its variation with pressure reflects non-ideal behavior
- Quantify non-ideal behavior by comparing computations of gas properties using the ideal gas law and the van der Waals equation

Thus far, the ideal gas law, $PV = nRT$, has been applied to a variety of different types of problems, ranging from reaction stoichiometry and empirical and molecular formula problems to determining the density and molar mass of a gas. As mentioned in the previous modules of this chapter, however, the behavior of a gas is often non-ideal, meaning that the observed relationships between its pressure, volume, and temperature are not accurately described by the gas laws. In this section, the reasons for these deviations from ideal gas behavior are considered.

One way in which the accuracy of $PV = nRT$ can be judged is by comparing the actual volume of 1 mole of gas (its molar volume, V_m) to the molar volume of an ideal gas at the same temperature and pressure. This ratio is called the **compressibility factor** (Z) with:

$$Z = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left(\frac{PV_m}{RT}\right)_{\text{measured}}$$

Ideal gas behavior is therefore indicated when this ratio is equal to 1, and any deviation from 1 is an indication of non-ideal behavior. Figure $2.1.4.1$shows plots of Z over a large pressure range for several common gases.

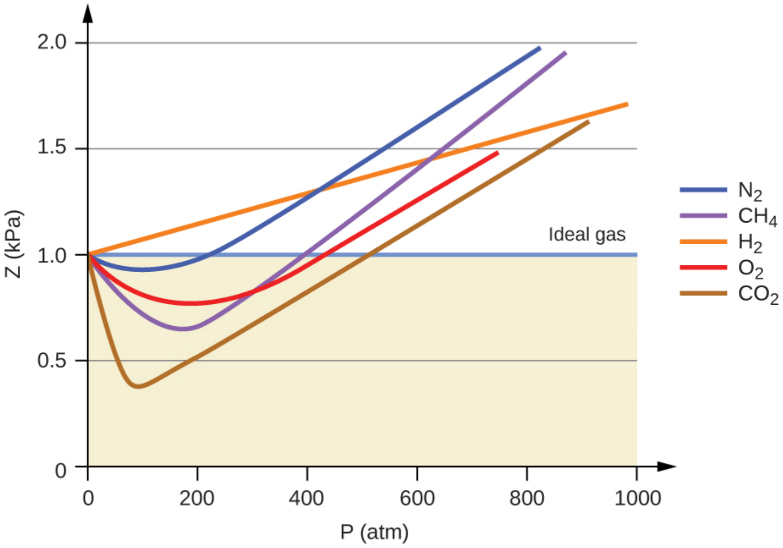


Figure $2.1.4.1$: A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law.

As is apparent from Figure $2.1.4.1$, the ideal gas law does not describe gas behavior well at relatively high pressures. To determine why this is, consider the differences between real gas properties and what is expected of a hypothetical ideal gas.

Particles of a hypothetical ideal gas have no significant volume and do not attract or repel each other. In general, real gases approximate this behavior at relatively low pressures and high temperatures. However, at high pressures, the molecules of a gas are crowded closer together, and the amount of empty space between the molecules is reduced. At these higher pressures, the volume of the gas molecules themselves becomes appreciable relative to the total volume occupied by the gas. The gas therefore becomes less compressible at these high pressures, and although its volume continues to decrease with increasing pressure, this decrease is not *proportional* as predicted by Boyle's law.

At relatively low pressures, gas molecules have practically no attraction for one another because they are (on average) so far apart, and they behave almost like particles of an ideal gas. At higher pressures, however, the force of attraction is also no longer insignificant. This force pulls the molecules a little closer together, slightly decreasing the pressure (if the volume is constant) or decreasing the volume (at constant pressure) (Figure 2.1.4.2). This change is more pronounced at low temperatures because the molecules have lower KE relative to the attractive forces, and so they are less effective in overcoming these attractions after colliding with one another.

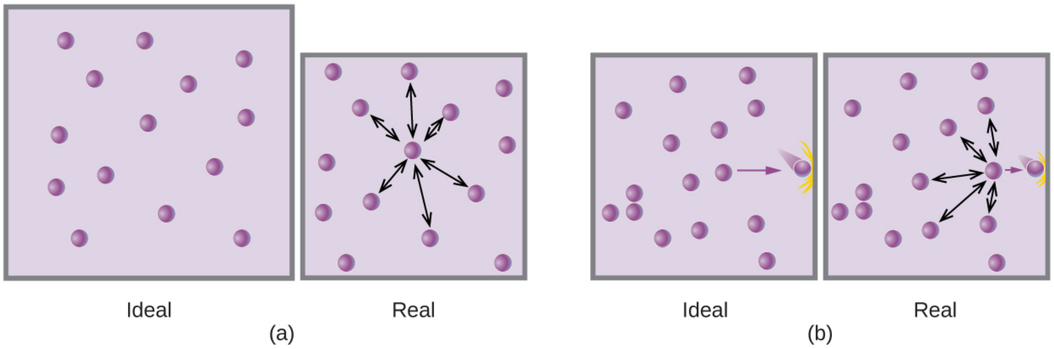


Figure 2.1.4.2: (a) Attractions between gas molecules serve to decrease the gas volume at constant pressure compared to an ideal gas whose molecules experience no attractive forces. (b) These attractive forces will decrease the force of collisions between the molecules and container walls, therefore reducing the pressure exerted at constant volume compared to an ideal gas.

There are several different equations that better approximate gas behavior than does the ideal gas law. The first, and simplest, of these was developed by the Dutch scientist Johannes van der Waals in 1879. The **van der Waals equation** improves upon the ideal gas law by adding two terms: one to account for the volume of the gas molecules and another for the attractive forces between them.

$$PV = nRT \longrightarrow \underbrace{\left(P + \frac{an^2}{V^2}\right)}_{\text{Correction for molecular attraction}} \underbrace{(V - nb)}_{\text{Correction for volume of molecules}} = nRT$$

The constant *a* corresponds to the strength of the attraction between molecules of a particular gas, and the constant *b* corresponds to the size of the molecules of a particular gas. The “correction” to the pressure term in the ideal gas law is

Table 2.1.4.1: Values of van der Waals Constants for Some Common Gases

Gas	a (L^2 atm/mol^2)	b (L/mol)
N_2	1.39	0.0391
O_2	1.36	0.0318
CO_2	3.59	0.0427
H_2O	5.46	0.0305
He	0.0342	0.0237
CCl_4	20.4	0.1383

At low pressures, the correction for intermolecular attraction, *a*, is more important than the one for molecular volume, *b*. At high pressures and small volumes, the correction for the volume of the molecules becomes important because the molecules themselves are incompressible and constitute an appreciable fraction of the total volume. At some intermediate pressure, the two corrections have opposing influences and the gas appears to follow the relationship given by $PV = nRT$ over a small range of pressures. This behavior is reflected by the “dips” in several of the compressibility curves shown in Figure 2.1.4.1. The attractive force between molecules initially makes the gas more compressible than an ideal gas, as pressure is raised (Z decreases with increasing *P*). At very high pressures, the gas becomes less compressible (Z increases with *P*), as the gas molecules begin to occupy an increasingly significant fraction of the total gas volume.

Strictly speaking, the ideal gas equation functions well when intermolecular attractions between gas molecules are negligible and the gas molecules themselves do not occupy an appreciable part of the whole volume. These criteria are satisfied under conditions of *low pressure and high temperature*. Under such conditions, the gas is said to behave ideally, and deviations from the gas laws are small enough that they may be disregarded—this is, however, very often not the case.

✓ Example 2.1.4.1: Comparison of Ideal Gas Law and van der Waals Equation

A 4.25-L flask contains 3.46 mol CO_2 at 229 °C. Calculate the pressure of this sample of CO_2:

a. from the ideal gas law
b. from the van der Waals equation
c. Explain the reason(s) for the difference.

Solution

(a) From the ideal gas law:

$$P=\frac{nRT}{V}=\frac{3.46\text{ mol}\times 0.08206 Eatmmol^{-1}K^{-1}\times 502K}{4.25I}=33.5atm$$

(b) From the van der Waals equation:

$$\left(P+\frac{n^2a}{V^2}\right)\times(V-nb)=nRT\longrightarrow P=\frac{nRT}{(V-nb)}-\frac{n^2a}{V^2}$$

$$P=\frac{3.46\text{ mol}\times 0.08206\text{ L atm mol}^{-1}\text{ K}^{-1}\times 502\text{ K}}{\left(4.25\text{ L}-3.46\text{ mol}\times 0.0427\text{ L mol}^{-1}\right)}-\frac{(3.46\text{ mol})^2\times 3.59\text{ L}^2\text{ atm mol}^2}{(4.24\text{ L})^2}$$

This finally yields P = 32.4 atm.

(c) This is not very different from the value from the ideal gas law because the pressure is not very high and the temperature is not very low. The value is somewhat different because CO_2 molecules do have some volume and attractions between molecules, and the ideal gas law assumes they do not have volume or attractions.

? Exercise 2.1.4.1

A 560-mL flask contains 21.3 g N_2 at 145 °C. Calculate the pressure of N_2:

a. from the ideal gas law
b. from the van der Waals equation
c. Explain the reason(s) for the difference.

Answer

(a) 46.562 atm; (b) 46.594 atm; (c) The van der Waals equation takes into account the volume of the gas molecules themselves as well as intermolecular attractions.

SECTION OVERVIEW

2.2: Thermodynamics

2.2.1: Energy Basics

Learning Objectives

By the end of this section, you will be able to:

- Define energy, distinguish types of energy, and describe the nature of energy changes that accompany chemical and physical changes
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

Chemical changes and their accompanying changes in energy are important parts of our everyday world (Figure $2.2.1.1$). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.


(a) (b) (c)

Figure $2.2.1.1$: The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by “Pink Sherbet Photography”/Flickr; credit b: modification of work by Jeffery Turner)

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world’s energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called thermochemistry. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. Food scientists use them to determine the energy content of foods. Biologists study the energetics of living organisms, such as the metabolic combustion of sugar into carbon dioxide and water. The oil, gas, and transportation industries, renewable energy providers, and many others endeavor to find better methods to produce energy for our commercial and personal needs. Engineers strive to improve energy efficiency, find better ways to heat and cool our homes, refrigerate our food and drinks, and meet the energy and cooling needs of computers and electronics, among other applications. Understanding thermochemical principles is essential for chemists, physicists, biologists, geologists, every type of engineer, and just about anyone who studies or does any kind of science.

Energy

Energy can be defined as the capacity to supply heat or do work. One type of work (w) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against the opposing force of the air already in the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: potential energy, the energy an object has because of its relative position, composition, or condition, and kinetic energy, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure 2.2.1.2). A battery has potential energy because the chemicals within it can produce electricity that can do work.

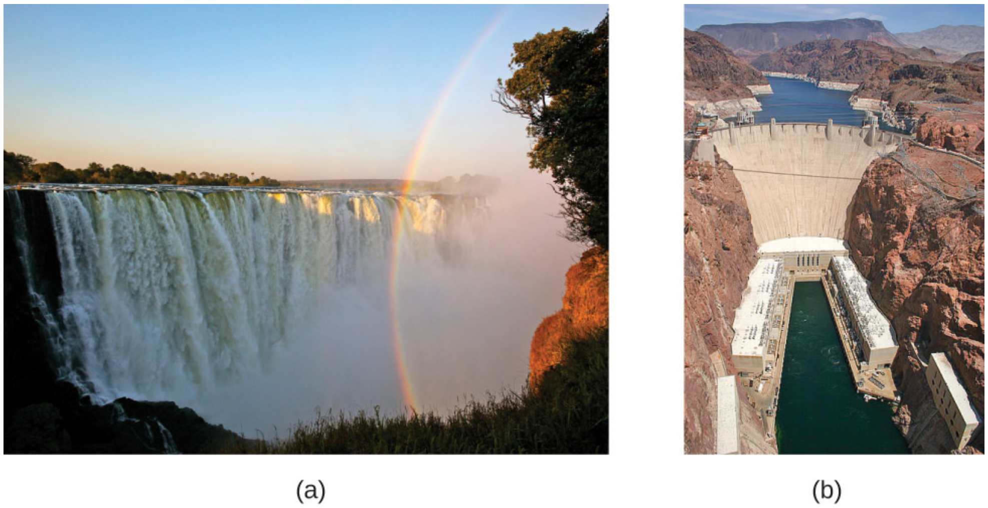

(a) (b)

Figure 2.2.1.2: (a) Water at a higher elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by “curimedia”/Wikimedia commons)

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car’s engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders’ pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry.

Thermal Energy, Temperature, and Heat

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of “hot” or “cold.” When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is “hot.” When the atoms and molecules are moving slowly, they have lower average KE, and we say that the object is “cold” (Figure 2.2.1.3). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

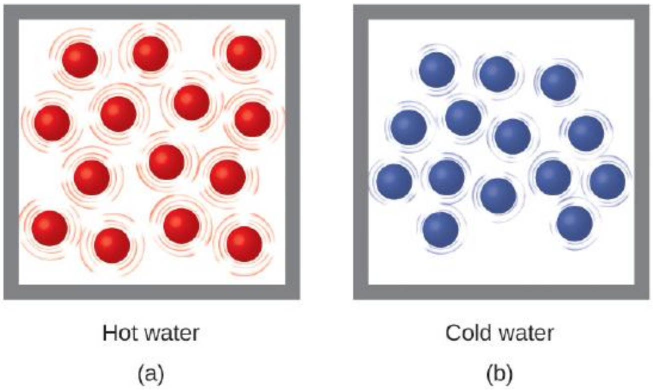


Figure 2.2.1.3: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Link to Learning

Click on this interactive simulation to view the effects of temperature on molecular motion.

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in Figure 2.2.1.4 The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

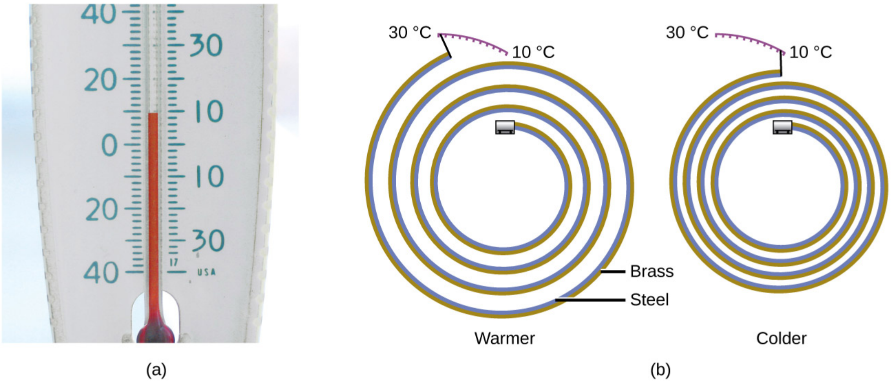


Figure 2.2.1.4: (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by “dwstucke”/Flickr)

Link to Learning

The following demonstration allows one to view the effects of heating and cooling a coiled bimetallic strip.

Heat (q) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature (Figure 2.2.1.5).

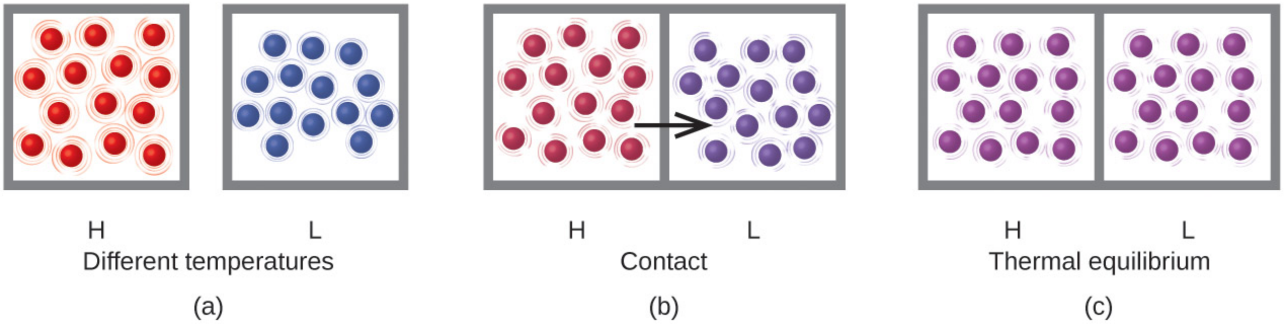


Figure 2.2.1.5: (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they contact each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature and their molecules have the same average kinetic energy.

Link to Learning

Click on the PhET simulation to explore energy forms and changes. Visit the Energy Systems tab to create combinations of energy sources, transformation methods, and outputs. Click on Energy Symbols to visualize the transfer of energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an exothermic process. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame (Figure 2.2.1.6). A reaction or change that absorbs heat is an endothermic process. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.

Figure 2.2.1.6: (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by "Skatebiker"/Wikimedia commons)

Historically, energy was measured in units of calories (cal). A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A joule (J) is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m^2/s^2, which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

We now introduce two concepts useful in describing heat flow and temperature change. The heat capacity (C) of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin):

$$C = \frac{q}{\Delta T}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an extensive property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C:

$$C_{\text{small pan}} = \frac{18,140 J}{50.0^{\circ} C} = 363 J/^{\circ} C$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

$$C_{\text{large pan}} = \frac{90,700 J}{50.0^{\circ} C} = 1814 J/^{\circ} C$$

The specific heat capacity (*c*) of a substance, commonly called its “specific heat,” is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

$$c = \frac{q}{m \Delta T}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

$$c_{\text{iron}} = \frac{18,140 J}{(808 g)(50.0^{\circ} C)} = 0.449 J/g^{\circ} C$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

$$c_{\text{iron}} = \frac{90,700 J}{(4040 g)(50.0^{\circ} C)} = 0.449 J/g^{\circ} C$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure 2.2.1.7).

Figure 2.2.1.7: Because of its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser)

Water has a relatively high specific heat (about 4.2 J/g °C for the liquid and 2.09 J/g °C for the solid); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table 2.2.1.1

Table 2.2.1.1: Specific Heats of Common Substances at 25 °C and 1 bar

Substance	Symbol (*state*)	Specific Heat (J/g °C)
helium	$He(g)$	5.193
water	$H_2O(l)$	4.184
ethanol	$C_2H_6O(l)$	2.376
ice	$H_2O(s)$	2.093 (at −10 °C)
water vapor	$H_2O(g)$	1.864
nitrogen	$N_2(g)$	1.040
air		1.007
oxygen	$O_2(g)$	0.918
aluminum	$Al(s)$	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	$Ar(g)$	0.522
iron	$Fe(s)$	0.449
copper	$Cu(s)$	0.385
lead	$Pb(s)$	0.130
gold	$Au(s)$	0.129
silicon	$Si(s)$	0.712

If we know the mass of a substance and its specific heat, we can determine the amount of heat, q, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

$$\begin{aligned} q &= (\text{ specific heat }) \times (\text{ mass of substance }) \times (\text{ temperature change }) \\ &= c \times m \times \Delta T \\ &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \end{aligned} \tag{2.2.1.1}$$

In this equation, c is the specific heat of the substance, m is its mass, and ΔT (which is read "delta T") is the temperature change, $T_{\text{final}} - T_{\text{initial}}$. If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a positive value, and the value of q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a negative value, and the value of q is negative.

✓ Example 2.2.1.1: Measuring Heat

A flask containing 8.0 10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 8.0 × 10^2 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need *800 times as much* to heat 8.0 × 10^2 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need *64 times as much* to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using Equation 2.2.1.1:

$$\begin{aligned} q &= c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}}) \\ &= \left(4.184 J/\frac{g}{\circ}{}^{\circ}C\right) \times \left(8.0 \times 10^2 g\right) \times (85 - 21)^{\circ}C \\ &= (4.184 J/g^{\circ}C) \times \left(8.0 \times 10^2 g\right) \times (64)^{\circ}C \\ &= 210,000 J \left(= 2.1 \times 10^2 kJ\right) \end{aligned}$$

Because the temperature increased, the water absorbed heat and *q* is positive.

? Exercise 2.2.1.1

How much heat, in joules, must be added to a 502 g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.449 J/g °C.

Answer

5.07 10^4 J

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

✓ Example 2.2.1.2: Determining Other Quantities

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C. Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship in Equation 2.2.1.1:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

Substituting the known values:

$$6640 J = c \times (348 g) \times (43.6 - 22.4)^{\circ}C$$

Solving:

$$c = \frac{6640 J}{(348 g) \times (21.2^{\circ}C)} = 0.900 J/g^{\circ}C$$

Comparing this value with the values in Table 2.2.1.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

? Exercise 2.2.1.2

A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C. Determine the specific heat of this metal, and predict its identity.

Answer

c = 0.451 J/g °C; the metal is likely to be iron

Chemistry in Everyday Life: Solar Thermal Energy Power Plants

The sunlight that reaches the earth contains thousands of times more energy than we presently capture. Solar thermal systems provide one possible solution to the problem of converting energy from the sun into energy we can use. Large-scale solar thermal plants have different design specifics, but all concentrate sunlight to heat some substance; the heat “stored” in that substance is then converted into electricity.

The Solana Generating Station in Arizona’s Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) (Figure 2.2.1.8). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.

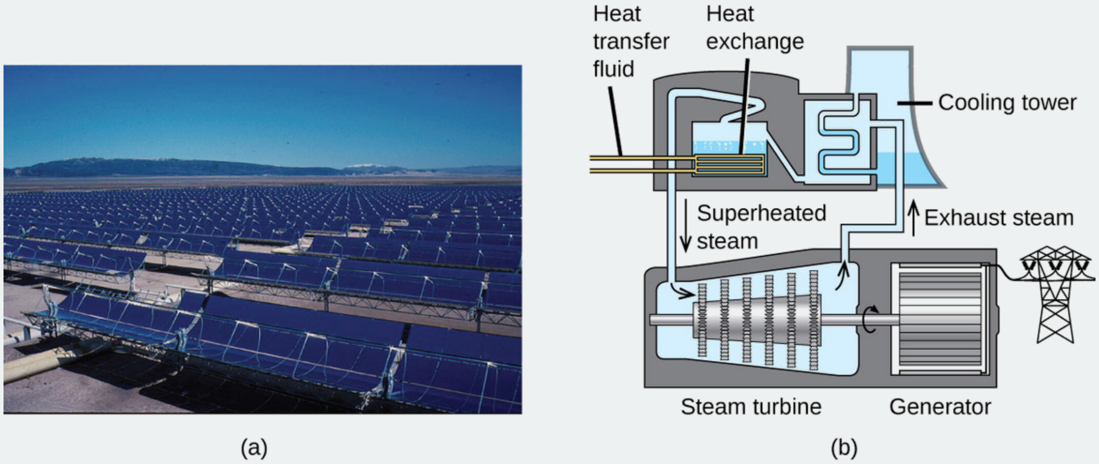


Figure 2.2.1.8: This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land Management)

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world (Figure 2.2.1.9). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as the working fluid because of its large heat capacity and heat of vaporization.

Figure 2.2.1.9: (a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border. (credit a: modification of work by Craig Dietrich; credit b: modification of work by “USFWS Pacific Southwest Region”/Flickr)

2.2.2: Enthalpy

Learning Objectives

By the end of this section, you will be able to:

- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function
- Write and balance thermochemical equations
- Calculate enthalpy changes for various chemical reactions
- Explain Hess’s law and use it to compute reaction enthalpies

Thermochemistry is a branch of chemical thermodynamics, the science that deals with the relationships between heat, work, and other forms of energy in the context of chemical and physical processes. As we concentrate on thermochemistry in this chapter, we need to consider some widely used concepts of thermodynamics.

Substances act as reservoirs of energy, meaning that energy can be added to them or removed from them. Energy is stored in a substance when the kinetic energy of its atoms or molecules is raised. The greater kinetic energy may be in the form of increased translations (travel or straight-line motions), vibrations, or rotations of the atoms or molecules. When thermal energy is lost, the intensities of these motions decrease and the kinetic energy falls. The total of all possible kinds of energy present in a substance is called the internal energy (U), sometimes symbolized as E.

As a system undergoes a change, its internal energy can change, and energy can be transferred from the system to the surroundings, or from the surroundings to the system. Energy is transferred into a system when it absorbs heat (q) from the surroundings or when the surroundings do work (w) on the system. For example, energy is transferred into room-temperature metal wire if it is immersed in hot water (the wire absorbs heat from the water), or if you rapidly bend the wire back and forth (the wire becomes warmer because of the work done on it). Both processes increase the internal energy of the wire, which is reflected in an increase in the wire’s temperature. Conversely, energy is transferred out of a system when heat is lost from the system, or when the system does work on the surroundings.

The relationship between internal energy, heat, and work can be represented by the equation:

$$\Delta U = q + w$$

as shown in Figure $2.2.2.1$ This is one version of the first law of thermodynamics, and it shows that the internal energy of a system changes through heat flow into or out of the system (positive q is heat flow in; negative q is heat flow out) or work done on or by the system. The work, w, is positive if it is done on the system and negative if it is done by the system.

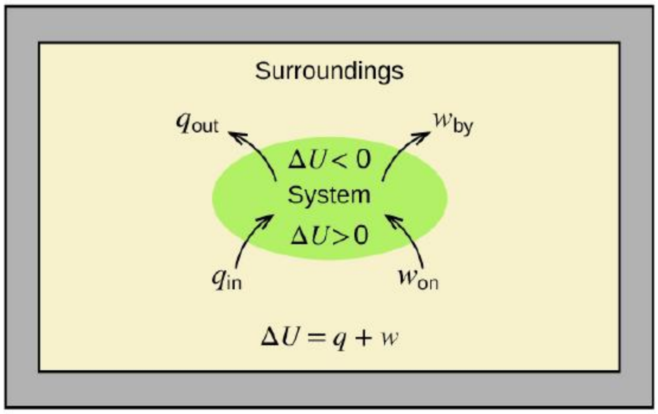


Figure $2.2.2.1$: The internal energy, U, of a system can be changed by heat flow and work. If heat flows into the system, q_{in}, or work is done on the system, w_{on}, its internal energy increases, $\Delta U > 0$. If heat flows out of the system, q_{out}, or work is done by the system, w_{by}, its internal energy decreases, $\Delta U < 0$.

A type of work called expansion work (or pressure-volume work) occurs when a system pushes back the surroundings against a restraining pressure, or when the surroundings compress the system. An example of this occurs during the operation of an internal combustion engine. The reaction of gasoline and oxygen is exothermic. Some of this energy is given off as heat, and some does work pushing the piston in the cylinder. The substances involved in the reaction are the system, and the engine and the rest of the universe are the surroundings. The system loses energy by both heating and doing work on the surroundings, and its internal energy decreases. (The engine is able to keep the car moving because this process is repeated many times per second while the engine is running.) We will consider how to determine the amount of work involved in a chemical or physical change in the chapter on thermodynamics.

Link to Learning

This view of an internal combustion engine illustrates the conversion of energy produced by the exothermic combustion reaction of a fuel such as gasoline into energy of motion.

As discussed, the relationship between internal energy, heat, and work can be represented as $\Delta U = q + w$. Internal energy is an example of a state function (or state variable), whereas heat and work are not state functions. The value of a state function depends only on the state that a system is in, and not on how that state is reached. If a quantity is not a state function, then its value *does* depend on how the state is reached. An example of a state function is altitude or elevation. If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5895 m, and it does not matter whether you hiked there or parachuted there. The distance you traveled to the top of Kilimanjaro, however, is not a state function. You could climb to the summit by a direct route or by a more roundabout, circuitous path (Figure 2.2.2.2). The distances traveled would differ (distance is not a state function) but the elevation reached would be the same (altitude is a state function).

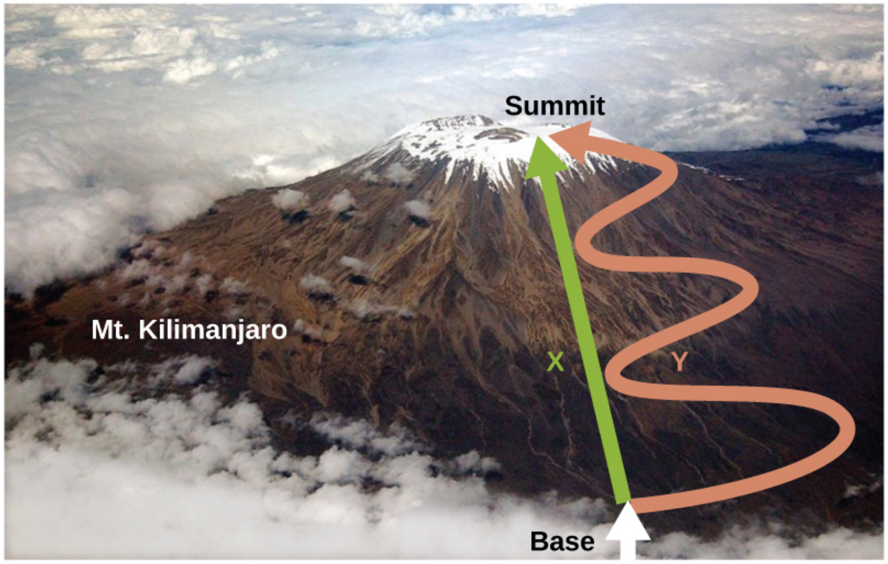


Figure 2.2.2.2: Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). (credit: modification of work by Paul Shaffner)

Chemists ordinarily use a property known as enthalpy (H) to describe the thermodynamics of chemical and physical processes. Enthalpy is defined as the sum of a system's internal energy (U) and the mathematical product of its pressure (P) and volume (V):

$$H = U + PV$$

Enthalpy is also a state function. Enthalpy values for specific substances cannot be measured directly; only enthalpy *changes* for chemical or physical processes can be determined. For processes that take place at constant pressure (a common condition for many chemical and physical changes), the enthalpy change (ΔH) is:

$$\Delta H = \Delta U + P\Delta V$$

The mathematical product $P\Delta V$ represents work (w), namely, expansion or pressure-volume work as noted. By their definitions, the arithmetic signs of ΔV and w will **always** be opposite:

$$P\Delta V = -w$$

Substituting this equation and the definition of internal energy into the enthalpy-change equation yields:

$$\begin{aligned}\Delta H &= \Delta U + P\Delta V \\ &= q_p + w - w \\ &= q_p\end{aligned}$$

where q_p is the **heat of reaction** under conditions of constant pressure.

And so, if a chemical or physical process is carried out at constant pressure with the only work done caused by expansion or contraction, then the heat flow (q_p) and enthalpy change (ΔH) for the process are equal.

The heat given off when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place, since it occurs at the essentially constant pressure of the atmosphere. On the other hand, the heat produced by a reaction measured in a bomb calorimeter is not equal to ΔH because the closed, constant-volume metal container prevents the pressure from remaining constant (it may increase or decrease if the reaction yields increased or decreased amounts of gaseous species). Chemists usually perform experiments under normal atmospheric conditions, at constant external pressure with $q = \Delta H$, which makes enthalpy the most convenient choice for determining heat changes for chemical reactions.

The following conventions apply when using ΔH:

- A negative value of an enthalpy change, $\Delta H < 0$, indicates an exothermic reaction; a positive value, $\Delta H > 0$, indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its ΔH is changed (a process that is endothermic in one direction is exothermic in the opposite direction).
- Chemists use a thermochemical equation to represent the changes in both matter and energy. In a thermochemical equation, the enthalpy change of a reaction is shown as a ΔH value following the equation for the reaction. This ΔH value indicates the amount of heat associated with the reaction involving the number of moles of reactants and products *as shown in the chemical equation*. For example, consider this equation:

  $$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H = -286 kJ$$

  This equation indicates that when 1 mole of hydrogen gas and mole of oxygen gas at some temperature and pressure change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released to the surroundings. If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must be multiplied by that same factor (ΔH is an extensive property):

  - two-fold increase in amounts

    $$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l) \quad \Delta H = 2 \times (-286 kJ) = -572 kJ$$

  - two-fold decrease in amounts

    $$\tfrac{1}{2}H_2(g) + \tfrac{1}{4}O_2(g) \longrightarrow \tfrac{1}{2}H_2O(l) \quad \Delta H = \frac{1}{2} \times (-286 kJ) = -143 kJ$$

- The enthalpy change of a reaction depends on the physical states of the reactants and products, so these must be shown. For example, when 1 mole of hydrogen gas and mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.

  $$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) \quad \Delta H = -242 kJ$$

✓ Example 2.2.2.1: Writing Thermochemical Equations

When 0.0500 mol of HCl(*aq*) reacts with 0.0500 mol of NaOH(*aq*) to form 0.0500 mol of NaCl(*aq*), 2.9 kJ of heat are produced. Write a balanced thermochemical equation for the reaction of one mole of HCl.

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

Solution

For the reaction of 0.0500 mol acid (HCl), $q = -2.9$ kJ. The reactants are provided in stoichiometric amounts (same molar ratio as in the balanced equation), and so the amount of acid may be used to calculate a molar enthalpy change. Since ΔH is an extensive property, it is proportional to the amount of acid neutralized:

$$\Delta H = 1 \ \text{mol}\,\cancel{HCl} \times \frac{-2.9kJ}{0.0500 \ \text{mol}\,\cancel{HCl}} = -58kJ$$

The thermochemical equation is then

$$\text{HCl(aq)} + \text{NaOH(aq)} \longrightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)} \quad \Delta H = -58kJ$$

Exercise 2.2.2.1

When 1.34 g Zn(*s*) reacts with 60.0 mL of 0.750 M HCl(*aq*), 3.14 kJ of heat are produced. Determine the enthalpy change per mole of zinc reacting for the reaction:

$$\text{Zn(s)} + 2\,\text{HCl(aq)} \longrightarrow \text{ZnCl}_2\text{(aq)} + \text{H}_2\text{(g)}$$

Answer

ΔH = −153 kJ

Be sure to take both stoichiometry and limiting reactants into account when determining the ΔH for a chemical reaction.

Example 2.2.2.2: Writing Thermochemical Equations

A gummy bear contains 2.67 g sucrose, $C_{12}H_{22}O_{11}$. When it reacts with 7.19 g potassium chlorate, $KClO_3$, 43.7 kJ of heat are produced. Write a thermochemical equation for the reaction of one mole of sucrose:

$$\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{(aq)} + 8\,\text{KClO}_3\text{(aq)} \longrightarrow 12\,\text{CO}_2\text{(g)} + 11\,\text{H}_2\text{O(l)} + 8\,\text{KCl(aq)}$$

Solution

Unlike the previous example exercise, this one does not involve the reaction of stoichiometric amounts of reactants, and so the *limiting reactant* must be identified (it limits the yield of the reaction and the amount of thermal energy produced or consumed).

The provided amounts of the two reactants are

$$(2.67\text{ g})\left(\frac{1\text{ mol}}{342.3\text{ g}}\right) = 0.00780\text{ mol C}_{12}\text{H}_{22}\text{O}_{11}$$

$$(7.19\text{ g})\left(\frac{1\text{ mol}}{122.5\text{ g}}\right) = 0.0587\text{ mol KCIO}$$

The provided molar ratio of perchlorate-to-sucrose is then

$$\frac{0.0587\text{ mol KCIO}_3}{0.00780\text{ mol C}_{12}\text{H}_{22}\text{O}_{11}} = 7.52$$

The balanced equation indicates 8 mol $KClO_3$ are required for reaction with 1 mol $C_{12}H_{22}O_{11}$. Since the provided amount of $KClO_3$ is less than the stoichiometric amount, it is the limiting reactant and may be used to compute the enthalpy change:

$$\Delta H = \frac{-43.7\text{ kJ}}{0.0587\text{ molKCIO}_3} = \frac{744\text{ kJ}}{\text{mol KCIO}_3}$$

Because the equation, as written, represents the reaction of 8 mol KClO_3, the enthalpy change is

$$\left(\frac{744\text{ kJ}}{1 \ \text{mol}\,\cancel{\text{KCIO}_3}}\right)\left(8 \ \text{mol}\,\cancel{\text{KCIO}_3}\right) = 5960\text{ kJ}$$

The enthalpy change for this reaction is −5960 kJ, and the thermochemical equation is:

$$\text{C}_{12}\text{H}_{22}\text{O}_{11} + 8\,\text{KClO}_3 \longrightarrow 12\,\text{CO}_2 + 11\,\text{H}_2\text{O} + 8\,\text{KCl} \quad \Delta H = -5960\text{ kJ}$$

Exercise 2.2.2.1

When 1.42 g of iron reacts with 1.80 g of chlorine, 3.22 g of $\mathrm{FeCl_2(s)}$ and 8.60 kJ of heat is produced. What is the enthalpy change for the reaction when 1 mole of $\mathrm{FeCl_2(s)}$ is produced?

Answer

ΔH = −338 kJ

Enthalpy changes are typically tabulated for reactions in which both the reactants and products are at the same conditions. A standard state is a commonly accepted set of conditions used as a reference point for the determination of properties under other different conditions. For chemists, the IUPAC standard state refers to materials under a pressure of 1 bar and solutions at 1 M, and does not specify a temperature. Many thermochemical tables list values with a standard state of 1 atm. Because the ΔH of a reaction changes very little with such small changes in pressure (1 bar = 0.987 atm), ΔH values (except for the most precisely measured values) are essentially the same under both sets of standard conditions. We will include a superscripted "o" in the enthalpy change symbol to designate standard state. Since the usual (but not technically standard) temperature is 298.15 K, this temperature will be assumed unless some other temperature is specified. Thus, the symbol is used to indicate an enthalpy change for a process occurring under these conditions. (The symbol ΔH is used to indicate an enthalpy change for a reaction occurring under nonstandard conditions.)

The enthalpy changes for many types of chemical and physical processes are available in the reference literature, including those for combustion reactions, phase transitions, and formation reactions. As we discuss these quantities, it is important to pay attention to the *extensive* nature of enthalpy and enthalpy changes. Since the enthalpy change for a given reaction is proportional to the amounts of substances involved, it may be reported on that basis (i.e., as the ΔH for specific amounts of reactants). However, we often find it more useful to divide one extensive property (ΔH) by another (amount of substance), and report a per-amount *intensive* value of ΔH, often "normalized" to a per-mole basis. (Note that this is similar to determining the intensive property specific heat from the extensive property heat capacity, as seen previously.)

Standard Enthalpy of Combustion

Standard enthalpy of combustion is the enthalpy change when 1 mole of a substance burns (combines vigorously with oxygen) under standard state conditions; it is sometimes called "heat of combustion." For example, the enthalpy of combustion of ethanol, −1366.8 kJ/mol, is the amount of heat produced when one mole of ethanol undergoes complete combustion at 25 °C and 1 atmosphere pressure, yielding products also at 25 °C and 1 atm.

$$\mathrm{C_2H_5OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2 + 3\,H_2O(l)} \quad \Delta H^\circ = -1366.8\,\mathrm{kJ}$$

Enthalpies of combustion for many substances have been measured; a few of these are listed in Table $2.2.2.1$. Many readily available substances with large enthalpies of combustion are used as fuels, including hydrogen, carbon (as coal or charcoal), and hydrocarbons (compounds containing only hydrogen and carbon), such as methane, propane, and the major components of gasoline.

Table $2.2.2.1$: Standard Molar Enthalpies of Combustion

Substance	Combustion Reaction	Enthalpy of Combustion, ΔH_c° (kJ/mol) at 25 °C
carbon	$C(s) + O_2(g) \longrightarrow CO_2(g)$	−393.5
hydrogen	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	−285.8
magnesium	$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$	−601.6
sulfur	$S(s) + O_2(g) \longrightarrow SO_2(g)$	−296.8
carbon monoxide	$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$	−283.0
methane	$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	−890.8
acetylene	$C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$	−1301.1
ethanol	$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$	−1366.8

Substance	Combustion Reaction	Enthalpy of Combustion, ΔH_c° (kJ/mol) at 25 °C
methanol	$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	−726.1
isooctane	$C_8H_{18}(l) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(l)$	−5461

✓ Example 2.2.2.3: Using Enthalpy of Combustion

As Figure 2.2.2.3 suggests, the combustion of gasoline is a highly exothermic process. Let us determine the approximate amount of heat produced by burning 1.00 L of gasoline, assuming the enthalpy of combustion of gasoline is the same as that of isooctane, a common component of gasoline. The density of isooctane is 0.692 g/mL.

Figure 2.2.2.3: The combustion of gasoline is very exothermic. (credit: modification of work by “AlexEagle”/Flickr)

Solution

Starting with a known amount (1.00 L of isooctane), we can perform conversions between units until we arrive at the desired amount of heat or energy. The enthalpy of combustion of isooctane provides one of the necessary conversions. Table 2.2.2.1 gives this value as −5460 kJ per 1 mole of isooctane (C_8H_{18}).

Using these data,

$$1.00\ \text{L}\,\cancel{\text{C}_8\text{H}_{18}} \times \left(\frac{1000\ \text{mL}\,\cancel{\text{C}_8\text{H}_{18}}}{1\ \text{L}\,\cancel{\text{C}_8\text{H}_{18}}}\right) \times \left(\frac{0.692\ \text{g}\,\cancel{\text{C}_8\text{H}_{18}}}{1\ \text{mL}\,\cancel{\text{C}_8\text{H}_{18}}}\right) \times \left(\frac{1\ \text{mol}\,\cancel{\text{C}_8\text{H}_{18}}}{114\ \text{g}\,\cancel{\text{C}_8\text{H}_{18}}}\right) \times \frac{-5460\ \text{kJ}}{1\ \text{mol}\,\cancel{\text{C}_8\text{H}_{18}}} = -3.31 \times 10^4\ \text{kJ}$$

The combustion of 1.00 L of isooctane produces 33,100 kJ of heat. (This amount of energy is enough to melt 99.2 kg, or about 218 lbs, of ice.)

Note: If you do this calculation one step at a time, you would find:

$$\begin{aligned} 1.00\ \text{L}\ \text{C}_8\text{H}_{18} &\longrightarrow 1.00 \times 10^3\ \text{mL}\text{C}_8\text{H}_{18} \\ 1.00 \times 10^3\ \text{mL}\ \text{C}_8\text{H}_{18} &\longrightarrow 692\ \text{g}\ \text{C}_8\text{H}_{18} \\ 692\ \text{g}\ \text{C}_8\text{H}_{18} &\longrightarrow 6.07\ \text{mol}\ \text{C}_8\text{H}_{18} \\ 6.07\ \text{mol}\ \text{C}_8\text{H}_{18} &\longrightarrow -3.31 \times 10^4 kJ \end{aligned}$$

? Exercise 2.2.2.3

How much heat is produced by the combustion of 125 g of acetylene?

Answer

6.25 10^3 kJ

Chemistry in Everyday Life: Emerging Algae-Based Energy Technologies (Biofuels)

As reserves of fossil fuels diminish and become more costly to extract, the search is ongoing for replacement fuel sources for the future. Among the most promising biofuels are those derived from algae (Figure 5.22). The species of algae used are nontoxic, biodegradable, and among the world's fastest growing organisms. About 50% of algal weight is oil, which can be readily converted into fuel such as biodiesel. Algae can yield 26,000 gallons of biofuel per hectare—much more energy per acre than other crops. Some strains of algae can flourish in brackish water that is not usable for growing other crops. Algae can produce biodiesel, biogasoline, ethanol, butanol, methane, and even jet fuel.

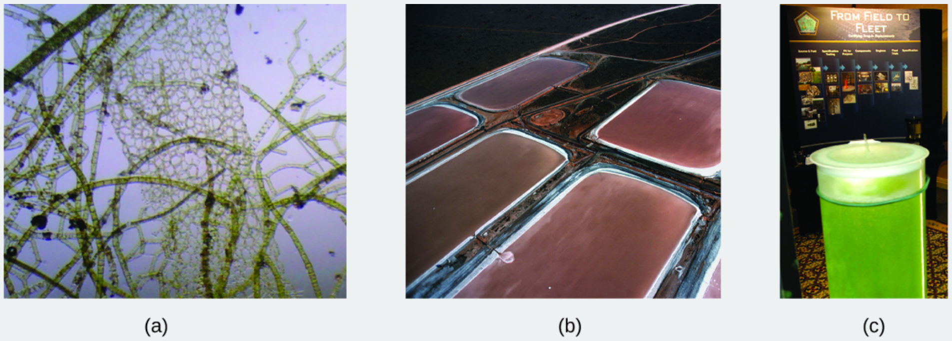


Figure 5.22 (a) Tiny algal organisms can be (b) grown in large quantities and eventually (c) turned into a useful fuel such as biodiesel. (credit a: modification of work by Micah Sittig; credit b: modification of work by Robert Kerton; credit c: modification of work by John F. Williams)

According to the US Department of Energy, only 39,000 square kilometers (about 0.4% of the land mass of the US or less than of the area used to grow corn) can produce enough algal fuel to replace all the petroleum-based fuel used in the US. The cost of algal fuels is becoming more competitive—for instance, the US Air Force is producing jet fuel from algae at a total cost of under \$5 per gallon.[3] The process used to produce algal fuel is as follows: grow the algae (which use sunlight as their energy source and CO_2 as a raw material); harvest the algae; extract the fuel compounds (or precursor compounds); process as necessary (e.g., perform a transesterification reaction to make biodiesel); purify; and distribute (Figure $2.2.2.4$).

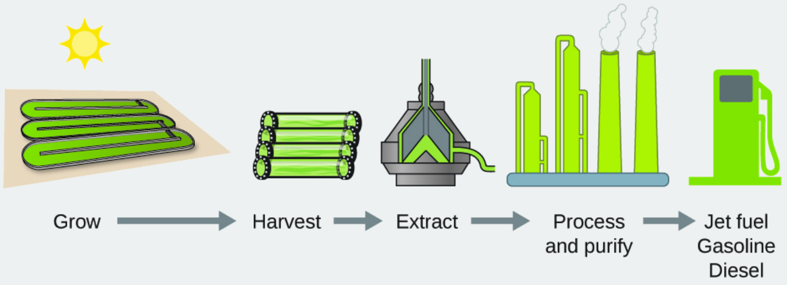


Figure $2.2.2.4$: Algae convert sunlight and carbon dioxide into oil that is harvested, extracted, purified, and transformed into a variety of renewable fuels.

Link to Learning

Click here to learn more about the process of creating algae biofuel.

Standard Enthalpy of Formation

A standard enthalpy of formation is an enthalpy change for a reaction in which exactly 1 mole of a pure substance is formed from free elements in their most stable states under standard state conditions. These values are especially useful for computing or predicting enthalpy changes for chemical reactions that are impractical or dangerous to carry out, or for processes for which it is difficult to make measurements. If we have values for the appropriate standard enthalpies of formation, we can determine the enthalpy change for any reaction, which we will practice in the next section on Hess's law.

The standard enthalpy of formation of $CO_2(g)$ is −393.5 kJ/mol. This is the enthalpy change for the exothermic reaction:

$$\mathrm{C(s)+O_2(g)\longrightarrow CO_2(g)}\quad \Delta H_f^\circ=\Delta H^\circ=-393.5\,\mathrm{kJ}$$

starting with the reactants at a pressure of 1 atm and 25 °C (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of CO_2, also at 1 atm and 25 °C. For nitrogen dioxide, $NO_2(g)$, is 33.2 kJ/mol. This is the enthalpy change for the reaction:

$$\tfrac{1}{2}\mathrm{N_2(g)} + \mathrm{O_2(g)} \longrightarrow \mathrm{NO_2(g)} \quad \Delta H_f^\circ = \Delta H^\circ = +33.2\ \mathrm{kJ}$$

A reaction equation with mole of $\mathrm{N_2}$ and 1 mole of $\mathrm{O_2}$ is correct in this case because the standard enthalpy of formation always refers to 1 mole of product, $\mathrm{NO_2(g)}$.

You will find a table of standard enthalpies of formation of many common substances in Appendix G. These values indicate that formation reactions range from highly exothermic (such as −2984 kJ/mol for the formation of $\mathrm{P_4O_{10}}$) to strongly endothermic (such as +226.7 kJ/mol for the formation of acetylene, $\mathrm{C_2H_2}$). By definition, the standard enthalpy of formation of an element in its most stable form is equal to zero under standard conditions, which is 1 atm for gases and 1 M for solutions.

Example 2.2.2.4: Evaluating an Enthalpy of Formation

Ozone, $\mathrm{O_3(g)}$, forms from oxygen, $\mathrm{O_2(g)}$, by an endothermic process. Ultraviolet radiation is the source of the energy that drives this reaction in the upper atmosphere. Assuming that both the reactants and products of the reaction are in their standard states, determine the standard enthalpy of formation, of ozone from the following information:

$$3\,\mathrm{O_2(g)} \longrightarrow 2\,\mathrm{O_3(g)} \quad \Delta H^\circ = +286\ \mathrm{kJ}$$

Solution

ΔH_f° is the enthalpy change for the formation of one mole of a substance in its standard state from the elements in their standard states. Thus, for $\mathrm{O_3(g)}$ is the enthalpy change for the reaction:

$$\tfrac{3}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{O_3(g)}$$

For the formation of 2 mol of $\mathrm{O_3(g)}$, $\Delta H^\circ = +286\ \mathrm{kJ}$. This ratio, can be used as a conversion factor to find the heat produced when 1 mole of $O_3(g)$ is formed, which is the enthalpy of formation for $\mathrm{O_3(g)}$:

$$\Delta H^\circ \text{ for 1 mole of } \mathrm{O_3}(g) = 1\ \mathrm{mol}\ \cancel{\mathrm{O_3}} \times \frac{286\ \mathrm{kJ}}{2\ \mathrm{mol\ O_3}} = 143\ \mathrm{kJ}$$

Therefore,

$$\Delta H_f^\circ\,[O_3(g)] = +143\ \mathrm{kJ/mol}.$$

Exercise 2.2.2.4

Hydrogen gas, $\mathrm{H_2}$, reacts explosively with gaseous chlorine, $\mathrm{Cl_2}$, to form hydrogen chloride, $\mathrm{HCl(g)}$. What is the enthalpy change for the reaction of 1 mole of $\mathrm{H_2(g)}$ with 1 mole of $\mathrm{Cl_2(g)}$ if both the reactants and products are at standard state conditions? The standard enthalpy of formation of $\mathrm{HCl(g)}$ is −92.3 kJ/mol.

Answer

For the reaction

$$\mathrm{H_2(g)} + \mathrm{Cl_2(g)} \longrightarrow 2\,\mathrm{HCl(g)} \quad \Delta H^\circ = -184.6\ \mathrm{kJ}$$

Example 2.2.2.5: Writing Reaction Equations for

Write the heat of formation reaction equations for:

a. $\mathrm{C_2H_5OH(l)}$
b. $\mathrm{Ca_3(PO_4)_2(s)}$

Solution

Remembering that reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:

a. $$2\,\mathrm{C(s, graphite)} + 3\,\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{C_2H_5OH(l)}$$

b. $$3\,\mathrm{Ca(s)} + \tfrac{1}{2}\mathrm{P_4(s)} + 4\,\mathrm{O_2(g)} \longrightarrow \mathrm{Ca_3(PO_4)_2(s)}$$

Note: The standard state of carbon is graphite, and phosphorus exists as $\mathrm{P_4}$.

Exercise 2.2.2.5

Write the heat of formation reaction equations for:

a. $\mathrm{C_2H_5OC_2H_5(l)}$
b. $\mathrm{Na_2CO_3(s)}$

Answer

a. $$4\,\mathrm{C(s, graphite)} + 5\,\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{C_2H_5OC_2H_5(l)}$$

b. $$2\,\mathrm{Na(s)} + \mathrm{C(s, graphite)} + \tfrac{3}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{Na_2CO_3(s)}$$

Hess's Law

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes. Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment.

This type of calculation usually involves the use of Hess's law, which states: *If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps*. Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish. For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process. The direct process is written:

$$\mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \quad \Delta H^\circ = -394 kJ$$

In the two-step process, first carbon monoxide is formed:

$$\mathrm{C(s)} + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{CO(g)} \quad \Delta H^\circ = -111 kJ$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$\mathrm{CO(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \quad \Delta H^\circ = -283 kJ$$

The equation describing the overall reaction is the sum of these two chemical changes:

$$\begin{array}{lrcl}
\text{step 1} & \mathrm{C(s)} + \tfrac{1}{2}\mathrm{O_2(g)} & \longrightarrow & \mathrm{CO(g)} \\
\text{step 2} & \mathrm{CO(g)} + \tfrac{1}{2}\mathrm{O_2(g)} & \longrightarrow & \mathrm{CO_2(g)} \\
\hline
\text{sum} & \mathrm{C(s)} + \cancel{\mathrm{CO(g)}} + \mathrm{O_2(g)} & \longrightarrow & \cancel{\mathrm{CO(g)}} + \mathrm{CO_2(g)}
\end{array}$$

Because the $\mathrm{CO(g)}$ produced in Step 1 is consumed in Step 2, the net change is:

$$\mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)}$$

According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps.

$$\begin{array}{llr}
\text{step 1} & C(s)+\frac{1}{2}O_2(g) \longrightarrow \cancel{CO(g)} & \Delta H^\circ = -111\,\text{kJ} \\
\text{step 2} & \cancel{CO(g)}+\frac{1}{2}O_2(g) \longrightarrow CO_2(g) & \Delta H^\circ = -283\,\text{kJ} \\
\hline
\text{sum} & C(s)+O_2(g) \longrightarrow CO_2(g) & \Delta H^\circ = -394\,\text{kJ}
\end{array}$$

The result is shown in Figure 2.2.2.5 We see that ΔH of the overall reaction is the same whether it occurs in one step or two. This finding (overall ΔH for the reaction = sum of ΔH values for reaction "steps" in the overall reaction) is true in general for chemical and physical processes.

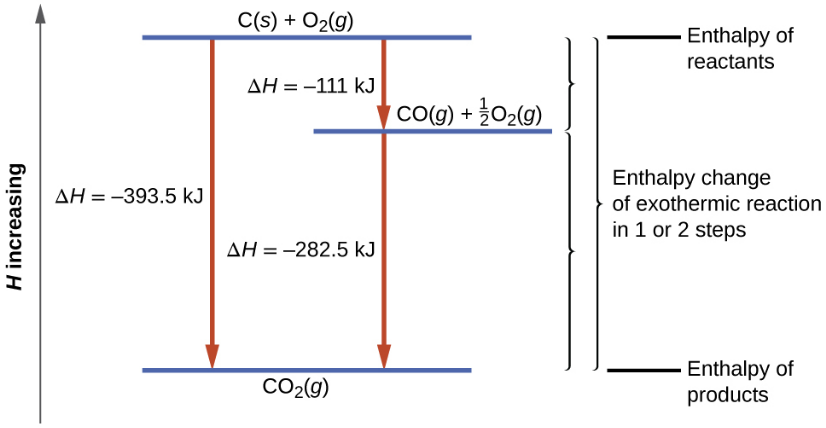


Figure 2.2.2.5: The formation of $CO_2(g)$ from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

Before we further practice using Hess's law, let us recall two important features of ΔH.

1. ΔH is directly proportional to the quantities of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of $NO_2(g)$ is +33.2 kJ:

   $$\frac{1}{2}N_2(g)+O_2(g) \longrightarrow NO_2(g) \quad \Delta H = +33.2\,\text{kJ}$$

   When 2 moles of NO_2 (twice as much) are formed, the ΔH will be twice as large:

   $$N_2(g)+2\,O_2(g) \longrightarrow 2\,NO_2(g) \quad \Delta H = +66.4\,\text{kJ}$$

   In general, if we multiply or divide an equation by a number, then the enthalpy change should also be multiplied or divided by the same number.

2. ΔH for a reaction in one direction is equal in magnitude and opposite in sign to ΔH for the reaction in the reverse direction. For example, given that:

   $$H_2(g)+Cl_2(g) \longrightarrow 2\,HCl(g) \quad \Delta H = -184.6\,\text{kJ}$$

   Then, for the "reverse" reaction, the enthalpy change is also "reversed":

✓ Example 2.2.2.6: Stepwise Calculation of Heat of Formation Using Hess's Law

Determine the enthalpy of formation, of $FeCl_3(s)$ from the enthalpy changes of the following two-step process that occurs under standard state conditions:

$$Fe(s)+Cl_2(g) \longrightarrow FeCl_2(s) \quad \Delta H^\circ = -341.8\,\text{kJ}$$

$$FeCl_2(s)+\frac{1}{2}Cl_2(g) \longrightarrow FeCl_3(s) \quad \Delta H^\circ = -57.7\,\text{kJ}$$

Solution

We are trying to find the standard enthalpy of formation of $FeCl_3(s)$, which is equal to ΔH° for the reaction:

$$Fe(s)+\frac{3}{2}Cl_2(g) \longrightarrow FeCl_3(s) \quad \Delta H_f^\circ = ?$$

Looking at the reactions, we see that the reaction for which we want to find ΔH° is the sum of the two reactions with known ΔH values, so we must sum their ΔH values:

$$\begin{array}{llll}
\text{step 1} & Fe(s) + Cl_2(g) \longrightarrow \cancel{FeCl_2(s)} & \Delta H^\circ & = -341.8\,kJ \\
\text{step 2} & \cancel{FeCl_2(s)} + \frac{1}{2}Cl_2(g) \longrightarrow FeCl_3(s) & \Delta H^\circ & = -57.7\,kJ \\
\hline
\text{sum} & Fe(s) + \frac{3}{2}Cl_2(g) \longrightarrow FeCl_3(s) & \Delta H^\circ & = -399.5\,kJ
\end{array}$$

The enthalpy of formation, ΔH_f° of $FeCl_3(s)$ is −399.5 kJ/mol.

? Exercise 2.2.2.6

Calculate ΔH for the process:

$$N_2(g) + 2\,O_2(g) \longrightarrow 2\,NO_2(g)$$

from the following information:

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \quad \Delta H = 180.5\,kJ$$

$$NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g) \quad \Delta H = -57.06\,kJ$$

Answer

66.4 kJ

Here is a less straightforward example that illustrates the thought process involved in solving many Hess's law problems. It shows how we can find many standard enthalpies of formation (and other values of ΔH) if they are difficult to determine experimentally.

✓ Example 2.2.2.7: A More Challenging Problem Using Hess's Law

Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

i. $$ClF(g) + F_2(g) \longrightarrow ClF_3(g) \quad \Delta H^\circ = ?$$

Use the reactions here to determine the ΔH^o for reaction (i):

ii. $$2\,OF_2(g) \longrightarrow O_2(g) + 2\,F_2(g) \quad \Delta H^\circ_{(ii)} = -49.4\,kJ$$

iii. $$2\,ClF(g) + O_2(g) \longrightarrow Cl_2O(g) + OF_2(g) \quad \Delta H^\circ_{(iii)} = +214.0\,kJ$$

iv. $$ClF_3(g) + O_2(g) \longrightarrow \frac{1}{2}Cl_2O(g) + \frac{3}{2}OF_2(g) \quad \Delta H^\circ_{(in)} = +236.2\,kJ$$

Solution

Our goal is to manipulate and combine reactions (ii), (iii), and (iv) such that they add up to reaction (i). Going from left to right in (i), we first see that ClF(g) is needed as a reactant. This can be obtained by multiplying reaction (iii) by $\frac{1}{2}$ which means that the ΔH^o change is also multiplied by $\frac{1}{2}$:

$$ClF(g) + \frac{1}{2}O_2(g) \longrightarrow \frac{1}{2}Cl_2O(g) + \frac{1}{2}OF_2(g) \quad \Delta H^\circ = \frac{1}{2}(214.0) = +107.0\,kJ$$

Next, we see that F_2 is also needed as a reactant. To get this, reverse and halve reaction *(ii)*, which means that the ΔH^o changes sign and is halved:

$$\frac{1}{2}O_2(g) + F_2(g) \longrightarrow OF_2(g) \quad \Delta H^\circ = +24.7\,kJ$$

To get ClF_3 as a product, reverse (iv), changing the sign of ΔH^o:

$$\frac{1}{2}Cl_2O(g) + \frac{3}{2}OF_2(g) \longrightarrow ClF_3(g) + O_2(g) \quad \Delta H^\circ = -236.2 kJ$$

Now check to make sure that these reactions add up to the reaction we want:

$$\begin{array}{llll}
\text{step 1} & ClF(g) + \cancel{\frac{1}{2}O_2(g)} & \longrightarrow \cancel{\frac{1}{2}Cl_2O(g)} + \cancel{\frac{1}{2}OF_2(g)} & \Delta H^\circ = +107.0\,kJ \\
\text{step 2} & \cancel{\frac{1}{2}O_2(g)} + F_2(g) & \longrightarrow \cancel{OF_2(g)} & \Delta H^\circ = +24.7\,kJ \\
\text{step 3} & \cancel{\frac{1}{2}Cl_2O(g)} + \cancel{\frac{3}{2}OF_2(g)} & \longrightarrow ClF_3(g) + \cancel{O_2(g)} & \Delta H^\circ = -236.2\,kJ \\
\hline
\text{sum} & ClF(g) + F_2(g) & \longrightarrow ClF_3(g) & \Delta H^\circ = -104.5\,kJ
\end{array}$$

Reactants $\frac{1}{2}O_2$ and $\frac{1}{2}O_2$ cancel out the product O_2; the $\frac{1}{2}Cl_2O$ product cancels $\frac{1}{2}Cl_2O$ reactant and $\frac{3}{2}Cl_2O$ reactant is cancelled by products $\frac{1}{2}OF_2$ and OF_2. This leaves only reactants $ClF(g)$ and $F_2(g)$ and product $ClF_3(g)$, which are what we want. Since summing these three modified reactions yields the reaction of interest, summing the three modified ΔH^o values will give the desired ΔH^o:

$$\Delta H^\circ = (+107.0 kJ) + (24.7 kJ) + (-236.2 kJ) = -104.5\,kJ$$

Exercise 2.2.2.7

Aluminum chloride can be formed from its elements:

i. $$2\,Al(s) + 3\,Cl_2(g) \longrightarrow 2\,AlCl_3(s) \quad \Delta H^\circ = ?$$

Use the reactions here to determine the ΔH^o for reaction *(i)*:

ii. $$HCl(g) \longrightarrow HCl(aq) \quad \Delta H^\circ_{(ii)} = -74.8\,kJ$$

iii. $$H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g) \quad \Delta H^\circ_{(iii)} = -185\,kJ$$

iv. $$AlCl_3(aq) \longrightarrow AlCl_3(s) \quad \Delta H^\circ_{(iv)} = +323\,kJ$$

v. $$2\,Al(s) + 6\,HCl(aq) \longrightarrow 2\,AlCl_3(aq) + 3\,H_2(g) \quad \Delta H^\circ_{(v)} = -1049\,kJ$$

Answer

−1407 kJ

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are:

i. decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by
ii. re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products).

The standard enthalpy change of the overall reaction is therefore equal to: (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants. This is usually rearranged slightly to be written as follows, with $\sum$ representing "the sum of" and n standing for the stoichiometric coefficients:

$$\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_f(\text{ products }) - \sum n \times \Delta H^\circ_f(\text{ reactants })$$

The following example shows in detail why this equation is valid, and how to use it to calculate the enthalpy change for a reaction of interest.

Example 2.2.2.8: Using Hess's Law

What is the standard enthalpy change for the reaction:

$$3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g) \quad \Delta H^\circ = ?$$

Solution: Using the Equation

Use the special form of Hess's law given previously, and values from Appendix G:

$$\begin{aligned}
\Delta H^\circ_{\text{reaction}} &= \sum n \times \Delta H^\circ_f(\text{ products }) - \sum n \times \Delta H^\circ_f(\text{ reactants })\\
&= \left[2\ \text{mol}\,\cancel{\text{HNO}_3(\text{aq})} \times \frac{-207.4\,\text{kJ}}{1\ \text{mol}\,\cancel{\text{HNO}_3(\text{aq})}} + 1\ \text{mol}\,\cancel{\text{NO(g)}} \times \frac{+90.2\,\text{kJ}}{1\ \text{mol}\,\cancel{\text{NO(g)}}}\right]\\
&\quad - \left[3\ \text{mol}\,\cancel{\text{NO}_2(\text{g})} \times \frac{+33.2\,\text{kJ}}{1\ \text{mole}\,\cancel{\text{NO}_2(\text{g})}} + 1\ \text{mol}\,\cancel{\text{H}_2\text{O(l)}} \times \frac{-285.8\,\text{kJ}}{1\ \text{mol}\,\cancel{\text{H}_2\text{O(l)}}}\right]\\
&= [2 \times (-206.64) + 90.25] - [3 \times 33.2 + -(-285.83)]\\
&= -323.03 + 186.23\\
&= -136.80\,\text{kJ}
\end{aligned}$$

Solution: Supporting Why the General Equation is Valid

Alternatively, we can write this reaction as the sum of the decompositions of $3\,\text{NO}_2(\text{g})$ and $H2O(l)$ into their constituent elements, and the formation of $2\,\text{HNO}_3(\text{aq})$ and $1\,\text{NO(g)}$ from their constituent elements. Writing out these reactions, and noting their relationships to the ΔH° values for these compounds (from Appendix G), we have:

$$\begin{aligned}
3\,\text{NO}_2(\text{g}) &\longrightarrow \tfrac{3}{2}\text{N}_2(\text{g}) + 3\,\text{O}_2(\text{g}) && \Delta H^\circ_1 = -99.6\,\text{kJ}\\
\text{H}_2\text{O(l)} &\longrightarrow \text{H}_2(\text{g}) + \tfrac{1}{2}\text{O}_2(\text{g}) && \Delta H^\circ_2 = +285.8\,\text{kJ}\ \left[-1 \times \Delta H^\circ_f\,(\text{H}_2\text{O})\right]\\
\text{H}_2(\text{g}) + \text{N}_2(\text{g}) + 3\,\text{O}_2(\text{g}) &\longrightarrow 2\,\text{HNO}_3(\text{aq}) && \Delta H^\circ_3 = -414.8\,\text{kJ}\ \left[2 \times \Delta H^\circ_f\,(\text{HNO}_3)\right]\\
\tfrac{1}{2}\text{N}_2(\text{g}) + \tfrac{1}{2}\text{O}_2(\text{g}) &\longrightarrow \text{NO(g)} && \Delta H^\circ_4 = +90.2\,\text{kJ}\ \left[1 \times \Delta H^\circ_f(\text{NO})\right]
\end{aligned}$$

Summing these reaction equations gives the reaction we are interested in:

$$3\,\text{NO}_2(\text{g}) + \text{H}_2\text{O(l)} \longrightarrow 2\,\text{HNO}_3(\text{aq}) + \text{NO(g)}$$

Summing their enthalpy changes gives the value we want to determine:

$$\begin{aligned}
\Delta H^\circ_{rxn} &= \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 + \Delta H^\circ_4\\
&= (-99.6\,\text{kJ}) + (+285.8\,\text{kJ}) + (-414.8\,\text{kJ}) + (+90.2\,\text{kJ})\\
&= -138.4\,\text{kJ}
\end{aligned}$$

So the standard enthalpy change for this reaction is ΔH° = −138.4 kJ.

Note that this result was obtained by:

a. multiplying the of each product by its stoichiometric coefficient and summing those values,
b. multiplying the of each reactant by its stoichiometric coefficient and summing those values, and then
c. subtracting the result found in (2) from the result found in (1).

This is also the procedure in using the general equation, as shown.

? Exercise 2.2.2.8

Calculate the heat of combustion of 1 mole of ethanol, $\text{C}_2\text{H}_5\text{OH(l)}$, when $\text{H}_2\text{O(l)}$ and $\text{CO}_2(\text{g})$ are formed. Use the following enthalpies of formation: $\text{C}_2\text{H}_5\text{OH(l)}$, −278 kJ/mol; $\text{H}_2\text{O(l)}$, −286 kJ/mol; and $\text{CO}_2(\text{g})$, −394 kJ/mol.

Answer

−1368 kJ/mol

Footnotes

- 3For more on algal fuel, see http://www.theguardian.com/environme...n-fuel-problem.

2.2.3: Spontaneity

Learning Objectives

By the end of this section, you will be able to:

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous 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. Iron exposed to the earth's atmosphere will corrode, but rust is not converted to iron without intentional chemical treatment. 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 $2.2.3.1$).

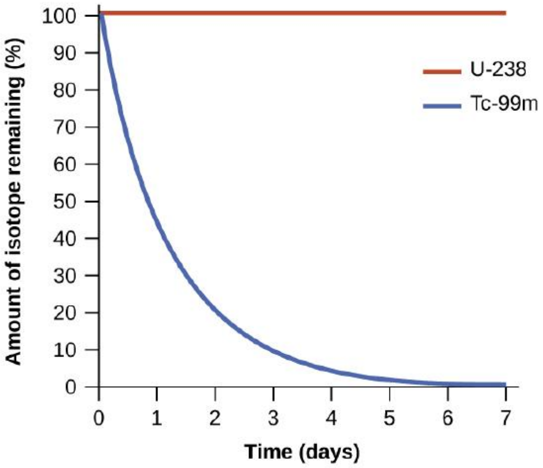


Figure $2.2.3.1$: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.

As another example, consider the conversion of diamond into graphite (Figure $2.2.3.2$).

$$C(s,\text{ diamond }) \longrightarrow C(s,\text{ graphite })$$

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; 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.

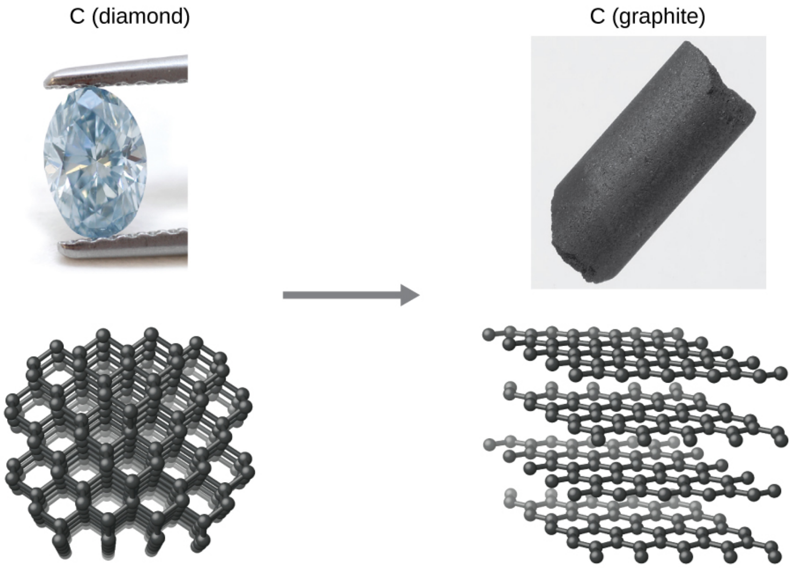


Figure $2.2.3.2$: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as *graphitization*, and its rate can be increased to easily measurable values at 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)

Dispersal of Matter and Energy

Extending the 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 in one flask and the other flask is empty ($P = 0$) (Figure $2.2.3.3$). When the valve is opened, the gas spontaneously expands to fill both flasks equally. 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=0 \quad \quad (P=0 \text { in a vacuum })|]

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.

$$\Delta U = q + w = 0 + 0 = 0$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the driving force 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 expansion took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

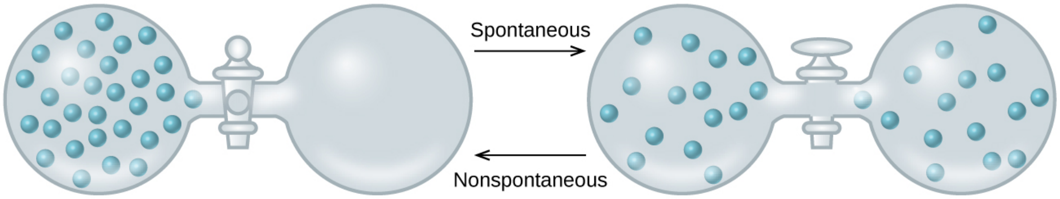


Figure $2.2.3.3$: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

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 $2.2.3.4$). 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.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0$$

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 2.2.3.4: When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

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 2.2.3.1: Redistribution of Matter during a Spontaneous Process

Describe how matter is 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

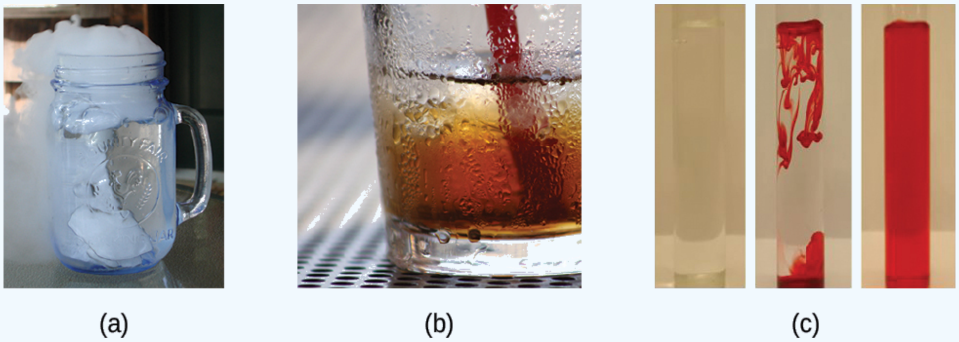


Figure 2.2.3.5: (credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Paul A. Flowers)

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.
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.
c. The process in question is diffusion. This process yields a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop of dye, zero in the water), and the final state of the system contains a single dye concentration throughout.

? Exercise 2.2.3.1

Describe how energy is redistributed when a spoon at room temperature is placed in a cup of hot coffee.

Answer

Heat will spontaneously flow from the hotter object (coffee) to the colder object (spoon), resulting in a more uniform distribution of thermal energy as the spoon warms and the coffee cools.

2.2.4: Entropy

Learning Objectives

By the end of this section, you will be able to:

- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure 2.2.4.1) published the results of an extensive study regarding the efficiency of steam heat engines. A later review of Carnot's findings by 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). In thermodynamics, a **reversible process** is one 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 in 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*.

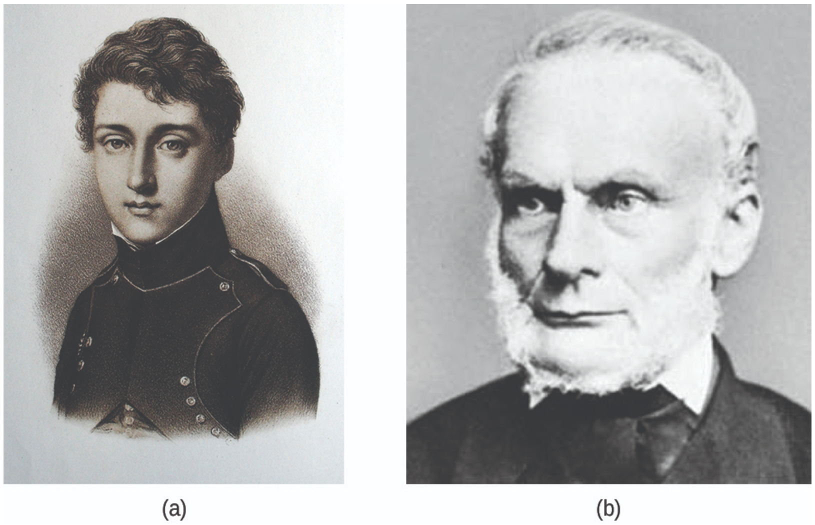


Figure 2.2.4.1: (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, 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:

$$\Delta S = \frac{q_{rev}}{T}$$

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.

Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the *number of microstates* (W) possible for the system. A **microstate** is a specific configuration of all the locations and energies of the atoms or molecules that make up a system. The relation between a system's entropy and the number of possible microstates is

$$S = k \ln W$$

where k is the Boltzmann constant, 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:

$$\Delta S=S_f-S_i=k\ln W_f-k\ln W_i=k\ln\frac{W_f}{W_i}$$

For processes involving an increase in the number of microstates, $W_f > W_i$, the entropy of the system increases and $\Delta S > 0$. 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 2.2.4.2 Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

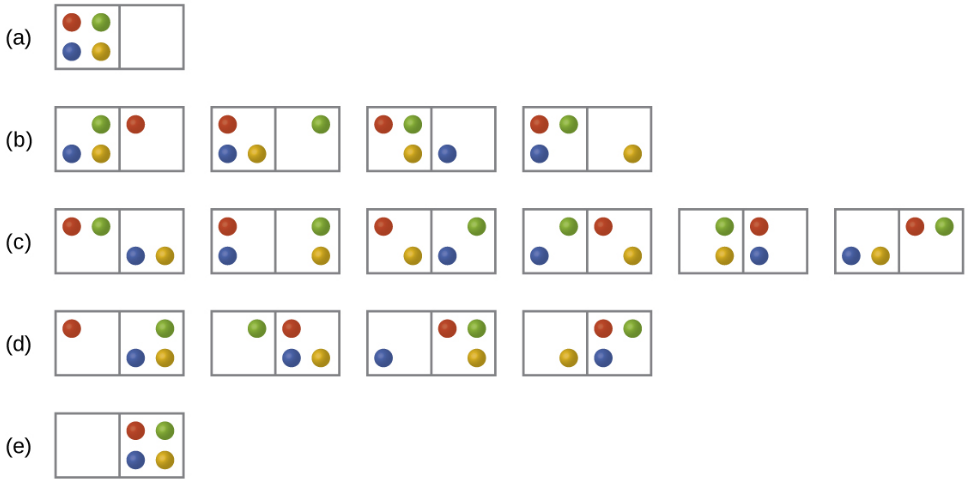


Figure 2.2.4.2: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is $\frac{6}{16}$ or $\frac{3}{8}$ The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of The probability of finding all particles in only one box (either the left box or right box) is then or

$$\left(\frac{1}{16}+\frac{1}{16}\right)=\frac{2}{16}\text{ or }\frac{1}{8}$$

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

This matter dispersal model of entropy is often described qualitatively in terms of the *disorder* of the system. By this description, microstates in which all the particles are in a single box are the most ordered, thus possessing the least entropy. Microstates in which the particles are more evenly distributed among the boxes are more disordered, possessing greater entropy.

The previous description of an ideal gas expanding into a vacuum (Figure 16.4) 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. Initially, the gas molecules are confined to just one of the two flasks. Opening the valve between the flasks increases the volume available to the gas molecules and, correspondingly, the number of microstates possible for the system. Since $W_f > W_i$, the expansion process involves an increase in entropy ($\Delta S > 0$) and is spontaneous.

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 thermal energy (represented as "*") in Figure 2.2.4.3 The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. Thus, 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 $\frac{4}{10}$. 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.

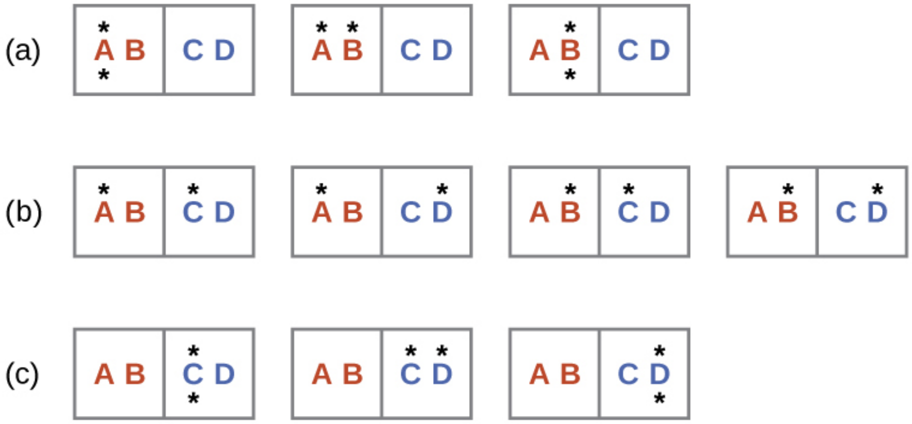
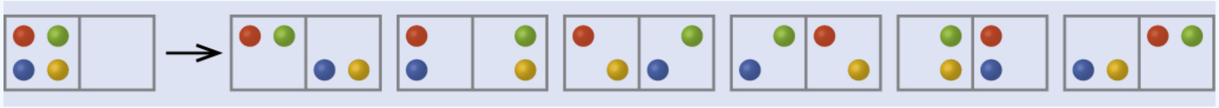


Figure 2.2.4.3: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

✓ Example 2.2.4.1: Determination of ΔS

Calculate the change in entropy for the process depicted below.



Solution

The initial number of microstates is one, the final six:

$$\Delta S = k \ln \frac{W_c}{W_a} = 1.38 \times 10^{-23} J/K \times \ln \frac{6}{1} = 2.47 \times 10^{-23} J/K$$

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 2.2.4.1

Consider the system shown in Figure 2.2.4.3 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

Predicting the Sign of Δ*S*

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 2.2.4.4 In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{\text{liquid}} > S_{\text{solid}}$ 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, $\Delta S < 0$.

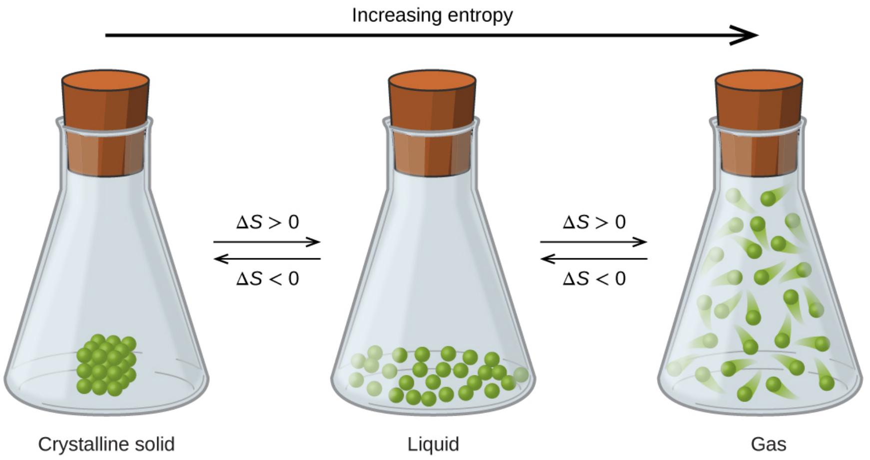


Figure 2.2.4.4: The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the gaseous phase, in which a given number of atoms or molecules occupy a *much* greater volume than in the liquid phase. Each atom or molecule can be found in many more locations, corresponding to a much greater number of microstates. 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 2.2.4.5).

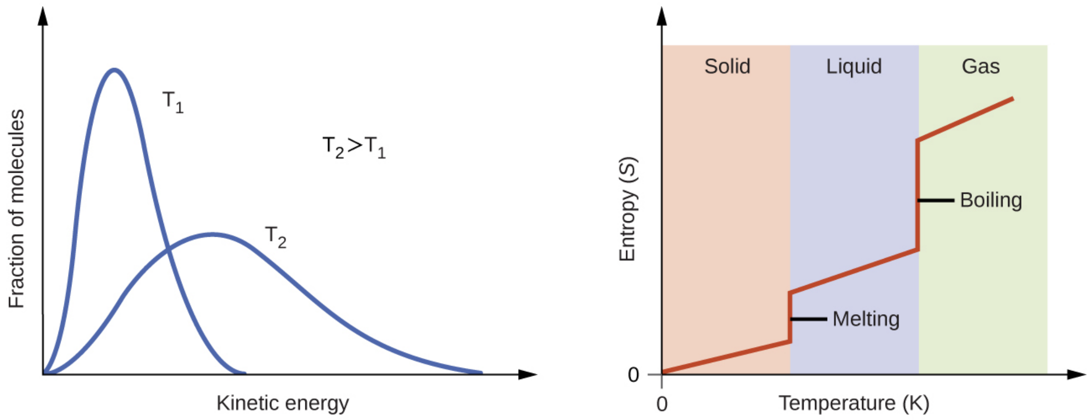


Figure 2.2.4.5: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance undergoes a phase transition, its entropy changes significantly.

Link to Learning

Try this simulator with interactive visualization of the dependence of particle location and freedom of motion on physical state and temperature.

The entropy of a substance is influenced by the 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 (a topic beyond the scope of this text). For molecules, greater numbers of atoms increase the number of ways in which the molecules can vibrate and thus the number of possible microstates and the entropy of the system.

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 2.2.4.2

Example 2.2.4.2: Predicting the Sign of ΔS

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

a. One mole liquid water at room temperature one mole liquid water at 50 °C
b. $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
c. \(C_6 H_6(l)+\frac{15}{2} O_2(g) \longrightarrow 6 CO_2(g)+3 H_2O(l))
d. $NH_3(s) \longrightarrow NH_3(l)$

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 2.2.4.1

Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

a. $NaNO_3(s) \longrightarrow Na^+(aq) + NO_3{}^-(aq)$
b. the freezing of liquid water
c. $CO_2(s) \longrightarrow CO_2(g)$
d. $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

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 increase in the amount of gaseous species.

2.2.5: The Second and Third Laws of Thermodynamics

Learning Objectives

By the end of this section, you will be able to:

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, a promising candidate has been identified: 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:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

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:

   $$\Delta S_{sys} = \frac{-q_{rev}}{T_{sys}} \quad \text{and} \quad \Delta S_{surr} = \frac{q_{rev}}{T_{surr}}$$

   The magnitudes of $-q_{\text{rev}}$ and q_{rev} are equal, their opposite arithmetic signs denoting loss of heat by the system and gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the entropy *decrease* of the system will be less than the entropy *increase* of the surroundings, and so *the entropy of the universe will increase*:

   $$|\Delta S_{\text{sys}}| < |\Delta S_{\text{surr}}|$$

   $$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

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:

   $$\Delta S_{sys} = \frac{q_{rev}}{T_{sys}} \quad \text{and} \quad \Delta S_{surr} = \frac{-q_{rev}}{T_{surr}}$$

   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 (that is, *the direction of the heat flow*) will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*
3. The objects are at essentially the same temperature, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the magnitudes of the entropy changes are essentially the same for both the system and the surroundings. In this case, the entropy change of the universe is zero, and the system is *at equilibrium*.

   $$|\Delta S_{\text{sys}}| \approx |\Delta S_{\text{surr}}|$$

   $$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

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 2.2.5.1.

Table 2.2.5.1: The Second Law of Thermodynamics

$\Delta S_{\text{univ}} > 0$	spontaneous

$\Delta S_{\text{univ}} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{\text{univ}} = 0$	at equilibrium

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:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \frac{q_{surr}}{T}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example $2.2.5.1$.

✓ Example 2.2.5.1: Will Ice Spontaneously Melt?

The entropy change for the process

$$H_2O(s) \longrightarrow H_2O(l)$$

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:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1 J/K + \frac{-6.00 \times 10^3 J}{263.15 K} = -0.7 J/K\end{aligned}$$

$S_{univ} < 0$, so melting is nonspontaneous (*not* spontaneous) at −10.0 °C.

At 10.00 °C (283.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1 J/K + \frac{-6.00 \times 10^3 J}{283.15 K} = +0.9 J/K\end{aligned}$$

$S_{\text{univ}} > 0$, so melting *is* spontaneous at 10.00 °C.

? Exercise 2.2.5.1

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, so $\Delta S_{\text{freezing}} = -\Delta S_{\text{melting}}$ = −22.1 J/K and q_{surr} = +6.00 kJ. At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

The Third Law of Thermodynamics

The previous section described the various contributions of matter and energy dispersal that contribute to the entropy of a system. With these contributions in mind, consider the entropy of a pure, perfectly crystalline solid possessing no kinetic energy (that is, at a temperature of absolute zero, 0 K). This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion means there is but one possible location for each identical atom or molecule comprising the crystal (W = 1). According to the Boltzmann equation, the entropy of this system is zero.

$$S = k \ln W = k \ln(1) = 0$$

This limiting condition for a system's entropy represents the third law of thermodynamics: *the entropy of a pure, perfect crystalline substance at 0 K is zero.*

Careful calorimetric measurements can be made to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. **Standard entropies** ($S°$) are for one mole of substance under standard conditions (a pressure of 1 bar and a temperature of 298.15 K; see details regarding standard conditions in the thermochemistry chapter of this text). The **standard entropy change** ($\Delta S°$) for a reaction may be computed using standard entropies as shown below:

$$\Delta S^{\circ} = \sum \nu S^{\circ}(\text{ products }) - \sum \nu S^{\circ}(\text{ reactants })$$

where ν represents stoichiometric coefficients in the balanced equation representing the process. For example, $\Delta S°$ for the following reaction at room temperature

$$mA + nB \longrightarrow xC + yD$$

is computed as:

$$= [xS^{\circ}(C) + yS^{\circ}(D)] - [mS^{\circ}(A) + nS^{\circ}(B)]$$

A partial listing of standard entropies is provided in Table $2.2.5.2$, and additional values are provided in Appendix G. The example exercises that follow demonstrate the use of $S°$ values in calculating standard entropy changes for physical and chemical processes.

Table $2.2.5.2$: Standard entropies for selected substances measured at 1 atm and 298.15 K. (Values are approximately equal to those measured at 1 bar, the currently accepted standard state pressure.)

Substance	**($\text{J mol}^{-1}\text{ K}^{-1}$)**
carbon	
C(*s*, graphite)	5.740
C(*s*, diamond)	2.38
$CO(g)$	197.7
$CO_2(g)$	213.8
$CH_4(g)$	186.3
$C_2H_4(g)$	219.5
$C_2H_6(g)$	229.5
$CH_3OH(l)$	126.8
$C_2H_5OH(l)$	160.7
hydrogen	
$H_2(g)$	130.57
$H(g)$	114.6
$H_2O(g)$	188.71
$H_2O(l)$	69.91
$HCl(g)$	186.8
$H_2S(g)$	205.7
oxygen	
$O_2(g)$	205.03

✓ Example 2.2.5.2: Determination of ΔS°

Calculate the standard entropy change for the following process:

$$H_2O(g) \longrightarrow H_2O(l)$$

Solution

Calculate the entropy change using standard entropies as shown above:

$$\Delta S^{\circ} = (1 mol)\left(70.0 J mol^{-1} K^{-1}\right) - (1 mol)\left(188.8 J mol^{-1} K^{-1}\right) = -118.8 J/K$$

The value for ΔS° is negative, as expected for this phase transition (condensation), which the previous section discussed.

? Exercise 2.2.5.2

Calculate the standard entropy change for the following process:

$$H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)$$

Answer

−120.6 J K^{-1} mol^{-1}

✓ Example 2.2.5.3: Determination of ΔS°

Calculate the standard entropy change for the combustion of methanol, CH_3OH:

$$2CH_3OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l)$$

Solution

Calculate the entropy change using standard entropies as shown above:

$$\begin{gathered} \Delta S^{\circ} = \sum \nu S^{\circ}(\text{ products }) - \sum \nu S^{\circ}(\text{ reactants }) \\ [2 mol \times S^{\circ}\,(CO_2(g)) + 4 mol \times S^{\circ}\,(H_2O(l))] - [2 mol \times S^{\circ}\,(CH_3OH(l)) + 3 mol \times S^{\circ}\,(O_2(g)]) \\ = \{[2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.2)]\} = -161.6 J/K \end{gathered}$$

? Exercise 2.2.5.3

Calculate the standard entropy change for the following reaction:

$$Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(l)$$

Answer

24.7 J/K

2.2.6: Free Energy

Learning Objectives

By the end of this section, you will be able to:

- 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
- Explain how temperature affects the spontaneity of some processes
- Relate standard free energy changes to equilibrium constants

One of the challenges of using the second law of thermodynamics to determine if a process is spontaneous is that it requires measurements of 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** (G) (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS$$

Free energy is a state function, and at constant temperature and pressure, the free energy change (ΔG) may be expressed as the following:

$$\Delta G = \Delta H - T\Delta S$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.)

The relationship between this system property and the spontaneity of a process may be understood by recalling the previously derived second law expression:

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T}$$

The first law requires that $q_{surr} = -q_{sys}$, and at constant pressure $q_{sys} = \Delta H$, so this expression may be rewritten as:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T}$$

Multiplying both sides of this equation by $-T$, and rearranging yields the following:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

Comparing this equation to the previous one for free energy change shows the following relation:

$$\Delta G = -T\Delta S_{\text{univ}}$$

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 $2.2.6.1$ summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Table 2.2.6.1: Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{univ} > 0$	$\Delta G < 0$	moves spontaneously in the forward direction, as written, to reach equilibrium
$\Delta S_{univ} < 0$	$\Delta G > 0$	nonspontaneous in the forward direction, as written, but moves spontaneously in the reverse direction, as written, to reach equilibrium
$\Delta S_{univ} = 0$	$\Delta G = 0$	reversible (at equilibrium)

What's "Free" about ΔG?

In addition to indicating spontaneity, the free energy change also provides information regarding the amount of useful work (w) that may be accomplished by a spontaneous process. Although a rigorous treatment of this subject is beyond the scope of an introductory chemistry text, a brief discussion is helpful for gaining a better perspective on this important thermodynamic property.

For this purpose, consider a spontaneous, exothermic process that involves a decrease in entropy. The free energy, as defined by

$$\Delta G = \Delta H - T\Delta S$$

may be interpreted as representing the difference between the energy produced by the process, ΔH, and the energy lost to the surroundings, $T\Delta S$. The difference between the energy produced and the energy lost is the energy available (or "free") to do useful work by the process, ΔG. If the process somehow could be made to take place under conditions of thermodynamic reversibility, the amount of work that could be done would be maximal:

$$\Delta G = w_{max}$$

where w_{max} refers to all types of work except expansion (pressure-volume) work.

However, as noted previously in this chapter, such conditions are not realistic. In addition, the technologies used to extract work from a spontaneous process (e.g., batteries) are never 100% efficient, and so the work done by these processes is always less than the theoretical maximum. Similar reasoning may be applied to a nonspontaneous process, for which the free energy change represents the *minimum* amount of work that must be done *on* the system to carry out the process.

Calculating Free Energy Change

Free energy is a state function, so its value depends only on the conditions of the initial and final states of the system. 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**, ΔG^o, according to the following relation.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

It is important to understand that for phase changes, ΔG° tells you if the phase change is spontaneous or not; will it happen, or not happen. For chemical reactions, ΔG° tells you the **extent** of a reaction. In other words, ΔG° for a reaction tells you how much product will be present at equilibrium. A reaction with $\Delta G^\circ < 0$ is considered **product-favored at equilibrium**; there will be more products than reactants when the reaction reaches equilibrium. A reaction with $\Delta G^\circ > 0$ is considered **reactant-favored at equilibrium**; there will be more reactants than products when the reaction reaches equilibrium.

✓ Example 2.2.6.1: Using Standard Enthalpy and Entropy Changes to Calculate ΔG°

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^o say about the spontaneity of this process?

Solution

The process of interest is the following:

$$H_2O(l) \longrightarrow H_2O(g)$$

The standard change in free energy may be calculated using the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

From Appendix G:

Substance	ΔH°_f (kJ/mol)	S° (kJ/K mol)
$H_2O(l)$	−285.83	70.0
$H_2O(g)$	−241.82	188.8

Using the appendix data to calculate the standard enthalpy and entropy changes yields:

$$\begin{aligned}
\Delta H^\circ &= \Delta H_f^\circ\left(\mathrm{H_2O(g)}\right) - \Delta H_f^\circ\left(\mathrm{H_2O(l)}\right) \\
&= [-241.82\ \mathrm{kJ/mol} - (-285.83)]\ \mathrm{kJ/mol} = 44.01\ \mathrm{kJ/mol} \\
\Delta S^\circ &= 1\ \mathrm{mol} \times S^\circ\left(\mathrm{H_2O(g)}\right) - 1\ \mathrm{mol} \times S^\circ\left(\mathrm{H_2O(l)}\right) \\
&= (1\ \mathrm{mol})\ 188.8 J/mol \cdot K - (1\ \mathrm{mol})\ 70.0\ \mathrm{J/mol\ K} = 118.8\ \mathrm{J\ /\ K} \\
\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ
\end{aligned}$$

Substitution into the standard free energy equation yields:

$$\begin{aligned}
\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\
&= 44.01\ \mathrm{kJ} - (298 K \times 118.8\ \mathrm{J/K}) \times \frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}} \\
&= 44.01\ \mathrm{kJ} - 35.4\ \mathrm{kJ} \\
&= 8.6\ \mathrm{kJ}
\end{aligned}$$

At 298 K (25 °C) so boiling is nonspontaneous (*not* spontaneous).

? Exercise 2.2.6.1

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 Δ*G*° say about the spontaneity of this process?

$$\mathrm{C_2H_6(g)} \longrightarrow \mathrm{H_2(g)} + \mathrm{C_2H_4(g)}$$

Answer

the reaction is nonspontaneous (*not* spontaneous) at 25 °C.

The standard free energy change for a reaction may also be calculated from **standard free energy of formation** ΔG_f^o values 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 enthalpy of formation, ΔG_f^o is by definition zero for elemental substances in their standard states. The approach used to calculate ΔG^o for a reaction from ΔG_f^o values is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction

$$mA + nB \longrightarrow xC + yD$$

the standard free energy change at room temperature may be calculated as

$$\begin{aligned}
\Delta G^\circ &= \sum \nu \Delta G^\circ(\text{ products }) - \sum \nu \Delta G^\circ(\text{ reactants }) \\
&= \left[x\Delta G_f^\circ(C) + y\Delta G_f^\circ(D)\right] - \left[m\Delta G_f^\circ(A) + n\Delta G_f^\circ(B)\right].
\end{aligned}$$

✓ Example 2.2.6.2: Using Standard Free Energies of Formation to Calculate ΔG°

Consider the decomposition of yellow mercury(II) oxide.

$$\mathrm{HgO(s, \backslash text\{yellow\})} \longrightarrow \mathrm{Hg(l)} + \tfrac{1}{2}\mathrm{O_2(g)}$$

Calculate the standard free energy change at room temperature, 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	$\Delta G_f^\circ(\mathrm{kJ\ /\ mol})$	$\Delta H_f^\circ(\mathrm{kJ\ /\ mol})$	$S^\circ(\mathrm{kJ\ /\ K\ mol})$

Compound	$\Delta G_f^\circ(\mathrm{kJ}\,/\,\mathrm{mol})$	$\Delta H_f^\circ(\mathrm{kJ}\,/\,\mathrm{mol})$	$S^\circ(\mathrm{kJ}\,/\,\mathrm{K\ mol})$
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:

$$\begin{aligned}\Delta G^\circ &= \sum \nu G_f^\circ(\text{ products }) - \sum \nu \Delta G_f^\circ(\text{ reactants }) \\ &= \left[1\Delta G_f^\circ\ \mathrm{Hg(l)} + \frac{1}{2}\Delta G_f^\circ\ \mathrm{O_2(g)}\right] - 1\Delta G_f^\circ\ \mathrm{HgO(s, yellow)} \\ &= \left[1\ \mathrm{mol}(0\ \mathrm{kJ}\,/\,\mathrm{mol}) + \frac{1}{2}\ \mathrm{mol}(0\ \mathrm{kJ}\,/\,\mathrm{mol})\right] - 1\ \mathrm{mol}(-58.43\ \mathrm{kJ}\,/\,\mathrm{mol}) = 58.43\ \mathrm{kJ}\,/\,\mathrm{mol}\end{aligned}$$

(b) Using enthalpies and entropies of formation:

$$\begin{aligned}\Delta H^\circ &= \sum \nu \Delta H_f^\circ(\text{ products }) - \sum \nu \Delta H_f^\circ(\text{ reactants }) \\ &= \left[1\Delta H_f^\circ\ \mathrm{Hg(l)} + \frac{1}{2}\Delta H_f^\circ\ \mathrm{O_2(g)}\right] - 1\Delta H_f^\circ\ \mathrm{HgO(s, yellow)} \\ &= \left[1\ \mathrm{mol}(0\ \mathrm{kJ}\,/\,\mathrm{mol}) + \frac{1}{2}\ \mathrm{mol}(0\ \mathrm{kJ}\,/\,\mathrm{mol})\right] - 1\ \mathrm{mol}(-90.46\ \mathrm{kJ}\,/\,\mathrm{mol}) = 90.46\ \mathrm{kJ}\,/\,\mathrm{mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \sum \nu \Delta S^\circ(\text{ products }) - \sum \nu \Delta S^\circ(\text{ reactants }) \\ &= \left[1\ \Delta S^\circ\ \mathrm{Hg(l)} + \frac{1}{2}\Delta S^\circ\ \mathrm{O_2(g)}\right] - 1\Delta S^\circ\ \mathrm{HgO(s, yellow)} \\ &= \left[1\ \mathrm{mol}(75.9\ \mathrm{J}\,/\,\mathrm{mol\ K}) + \frac{1}{2}\ \mathrm{mol}(205.2\ \mathrm{J}\,/\,\mathrm{mol\ K})\right] - 1\mathrm{mol}(71.13\ \mathrm{J}\,/\,\mathrm{mol\ K}) = 107.4\ \ \mathrm{J}\,/\,\mathrm{mol\ K}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 90.46\ \mathrm{kJ} - 298.15\ \mathrm{K} \times 107.4\ \mathrm{J}\,/\,\mathrm{K\cdot mol} \times \frac{1\ \ \mathrm{kJ}}{1000\ \mathrm{J}} \\ &= (90.46 - 32.01)\ \mathrm{kJ}\,/\,\mathrm{mol} = 58.45\ \mathrm{kJ}\,/\,\mathrm{mol}\end{aligned}$$

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 2.2.6.1

Calculate $\Delta G°$ 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?

$$\mathrm{C_2H_4(g) \longrightarrow H_2(g) + C_2H_2(g)}$$

Answer

a. 140.8 kJ/mol, nonspontaneous
b. 141.5 kJ/mol, nonspontaneous

Free Energy Changes for Coupled Reactions

The use of free energies of formation to compute free energy changes for reactions as described above is possible because ΔG is a state function, and the approach is analogous to the use of Hess' Law in computing enthalpy changes (see the chapter on thermochemistry). Consider the vaporization of water as an example:

$$\mathrm{H_2O(l)} \longrightarrow \mathrm{H_2O(g)}$$

An equation representing this process may be derived by adding the formation reactions for the two phases of water (necessarily reversing the reaction for the liquid phase). The free energy change for the sum reaction is the sum of free energy changes for the two added reactions:

$$\begin{array}{ll}
\mathrm{H_2(g)} + \frac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{H_2O(g)} & \Delta G^\circ_f \text{ gas} \\
\mathrm{H_2O(l)} \longrightarrow \mathrm{H_2(g)} + \frac{1}{2}\mathrm{O_2(g)} & -\Delta G^o_f \text{ liquid} \\
\hline
\mathrm{H_2O(l)} \longrightarrow \mathrm{H_2O(g)} & \Delta G^\circ = \Delta G^\circ_f \text{ gas} - \Delta G^\circ_f \text{ liquid}
\end{array}$$

This approach may also be used in cases where a nonspontaneous reaction is enabled by coupling it to a spontaneous reaction. For example, the production of elemental zinc from zinc sulfide is thermodynamically unfavorable, as indicated by a positive value for ΔG^o:

$$\mathrm{ZnS(s)} \rightarrow \mathrm{Zn(s)} + \mathrm{S(s)} \quad \Delta G^\circ_1 = 201.3kJ$$

The industrial process for production of zinc from sulfidic ores involves coupling this decomposition reaction to the thermodynamically favorable oxidation of sulfur:

$$\mathrm{S(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{SO_2(g)} \quad \Delta G^\circ_2 = -300.1kJ$$

The coupled reaction exhibits a negative free energy change and is spontaneous:

$$\mathrm{ZnS(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{Zn(s)} + \mathrm{SO_2(g)}$$

$$\Delta G^\circ = 201.3 \text{ kJ} + -300.1 \text{ kJ} = -98.8 \text{ kJ}$$

This process is typically carried out at elevated temperatures, so this result obtained using standard free energy values is just an estimate. The gist of the calculation, however, holds true.

✓ Example 2.2.6.3: Calculating Free Energy Change for a Coupled Reaction

Is a reaction coupling the decomposition of ZnS to the formation of $\mathrm{H_2S}$ expected to be spontaneous under standard conditions?

Solution

Following the approach outlined above and using free energy values from Appendix G:

$$\begin{array}{lrr}
\text{Decomposition of zinc sulfide:} & \mathrm{ZnS(s)} \rightarrow \mathrm{Zn(s)} + \mathrm{S(s)} & \Delta G^\circ_1 = 201.3 \text{ kJ} \\
\text{Formation of hydrogen sulfide:} & \mathrm{S(s)} + \mathrm{H_2(g)} \rightarrow \mathrm{H_2S(g)} & \Delta G^\circ_1 = -33.4 \text{ kJ} \\
\hline
\text{Coupled reaction:} & \mathrm{ZnS(s)} + \mathrm{H_2(g)} \rightarrow \mathrm{Zn(s)} + \mathrm{H_2S(g)} & \Delta G^\circ = 201.3 \text{ kJ} + -33.4 \text{ kJ} = 167.9 \text{ kJ}
\end{array}$$

The coupled reaction exhibits a positive free energy change and is thus nonspontaneous.

? Exercise 2.2.6.3

What is the standard free energy change for the reaction below? Is the reaction expected to be spontaneous under standard conditions?

$$\mathrm{FeS(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{Fe(s)} + \mathrm{SO_2(g)}$$

Answer

−199.7 kJ; spontaneous

Temperature Dependence of Spontaneity and Extent of Reaction

As was previously demonstrated in this chapter's section on entropy, 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. In a similar, but not identical fashion, some chemical reactions can switch from being product-favored at equilibrium, to being reactant-favored at equilibrium, depending on the temperature.

> **Note**
>
> The numerical value of ΔG° is always dependent on the temperature. In this section we are determining whether or not the **sign** of ΔG° is dependent on the temperature.

To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The extent of a process, as reflected in the arithmetic sign of its standard 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^o and ΔS^o are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, ΔG^o will be negative if the magnitude of the $T\Delta S^o$ term is greater than ΔH^o. If the $T\Delta S^o$ term is less than ΔH^o, the free energy change will be positive. Such a process is *product-favored at equilibrium at high temperatures and reactant-favored at equilibrium at low temperatures.*
2. **Both ΔH^o and ΔS^o are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, ΔG^o will be negative if the magnitude of the $T\Delta S^o$ term is less than ΔH^o. If the $T\Delta S^o$ term's magnitude is greater than ΔH^o, the free energy change will be positive. Such a process is *product-favored at equilibrium at low temperatures* and *reactant-favored at equilibrium at high temperatures.*
3. **ΔH^o is positive and ΔS^o is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, ΔG^o will be positive regardless of the temperature. Such a process is *reactant-favored at equilibrium at all temperatures.*
4. **ΔH^o is negative and ΔS^o is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, ΔG^o will be negative regardless of the temperature. Such a process is *product-favored at equilibrium at all temperatures.*

These four scenarios are summarized in Table 2.2.6.1

Table 2.2.6.1

Sign of ΔH^o	Sign of ΔS^o	Sign of ΔG^o	Temperature Dependence of ΔG^o
-	+	-	The sign of ΔG^o does not depend on the temperature.The reaction is product-favored at equilibrium at all temperatures.
+	-	+	The sign of ΔG^o does not depend on the temperature.The reaction is reactant-favored at equilibrium at all temperatures.
-	-	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.
+	+	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.

Example 2.2.6.3: Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2\,\mathrm{C}(s)+\mathrm{O_2}(g)\longrightarrow 2\,\mathrm{CO}(g)$$

Does the sign of ΔG° of this process depend upon temperature?

Solution

Combustion processes are exothermic ($\Delta H^{\circ}<0$). 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, $\Delta S^{\circ}>0$). The reaction is therefore product-favored at equilibrium ($\Delta G^{\circ}<0$) at all temperatures.

Exercise 2.2.6.3

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\,\mathrm{Fe}(s)+3\,\mathrm{O_2}(g)\longrightarrow 2\,\mathrm{Fe_2O_3}(s)$$

Does the sign of ΔG^o of this process depend upon temperature?

Answer

ΔH^o and ΔS^o are both negative; the reaction is product-favored at equilibrium at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of the sign of ΔG^o, 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 reactant-favored at equilibrium at one temperature but product-favored at equilibrium at another temperature will necessarily undergo a change in “extent” (as reflected by its ΔG^o) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which ΔG^o is plotted on the *y* axis versus *T* on the *x* axis:

$$\Delta G^{\circ}=\Delta H^{\circ}-T\Delta S^{\circ}$$

$$y=b+mx$$

Such a plot is shown in Figure 2.2.6.2 A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependence for the sign of ΔG^o as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG^o) 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^o is zero:

$$\Delta G^{\circ}=0=\Delta H^{\circ}-T\Delta S^{\circ}$$

$$T=\frac{\Delta H^{\circ}}{\Delta S^{\circ}}$$

Thus, saying a process is product-favored at equilibrium at “high” or “low” temperatures means the temperature is above or below, respectively, that temperature at which ΔG^o for the process is zero.

Note

In this discussion, we have used two different descriptions for the meaning of the sign of ΔG^o. You should be aware of the meaning of each description.

a) **Extent of Reaction:** This description is used to predict the ratio of the product and reactant concentrations at equilibrium. In this description, we use the thermodynamic term ΔG^o to tell us the same information as the equilibrium constant, K. When $\Delta G^o < 0$, K > 1, and the reaction will be product-favored at equilibrium. When $\Delta G^o > 0$, K< 1, and the reaction is reactant-favored at equilibrium. When ΔG^o = 0, K =1, and the reaction will have roughly equal amounts of products and reactants at equilibrium. In all cases, the reaction will form a mixture of products and reactants at equilibrium. We use the sign and magnitude of ΔG^o to tell us how much product will be made if the reaction is allowed to reach equilibrium.

b) **Spontaneity:** This description is much more complicated because it involves two different interpretations of how a reaction at standard state occurs. One interpretation involves the hypothetical process in which the reaction proceeds from a starting point of pure reactants to a finishing point of pure products, with all substances isolated in their own containers under standard state conditions. In the second, more realistic interpretation, the reaction starts with all reactants and all products in their standard state in one container. We then allow this specific mixture to react an infinitesimally small amount so that we can obtain a rate of change in free energy with respect to the extent of reaction when all reactants and products are mixed and (essentially) in their standard states. Although each interpretation describes a different reaction scenario, the value of the difference in free energy and the value of the rate of change in free energy are the same number. If $\Delta G^o < 0$, we say that the reaction is spontaneous, meaning that the reaction would proceed in the forward direction, as written, to form pure products in their standard state. If $\Delta G^o > 0$, we say that the reaction is nonspontaneous, meaning that the reaction would proceed in the reverse direction, as written, to form pure reactants in their standard state. If $\Delta G^o = 0$, we say that the neither the reactants nor the products are favored to be formed.

A detailed treatment of the meaning of ΔG° can be found in the paper, "Free Energy versus Extent of Reaction" by Richard S. Treptow, Journal of Chemical Education, **1996**, Volume 73 (1), 51-54.

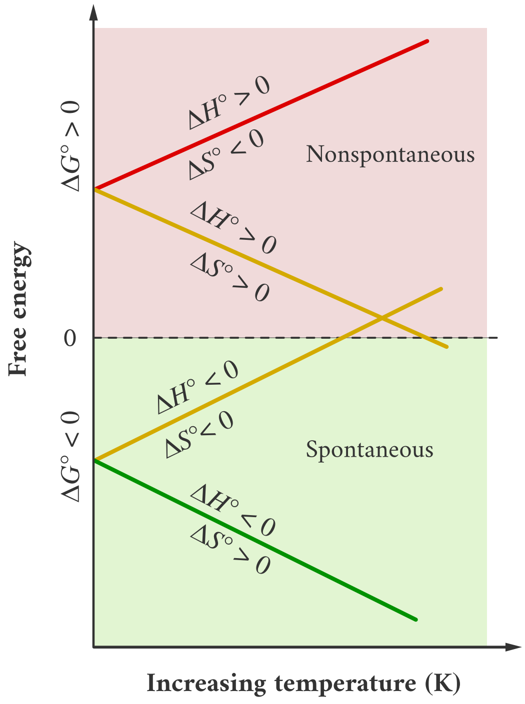


Figure 2.2.6.2: These plots show the variation in ΔG° with temperature for the four possible combinations of arithmetic sign for ΔH° and ΔS°. Note that in this graph of ΔG°, "spontaneous" is synonymous with "product-favored at equilibrium", and "nonspontaneous" is synonymous with "reactant-favored at equilibrium".

✓ Example 2.2.6.4: 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 Tables T1 or T2 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 Tables T1 or T2,

$$\begin{aligned}\Delta H^\circ &= \Delta H_\mathrm{f}^\circ(H_2O(g)) - \Delta H_\mathrm{f}^\circ(H_2O(l)) \\ &= -241.82\ \mathrm{kJ/mol} - (-285.83\ \mathrm{kJ/mol}) = 44.01\ \mathrm{kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \Delta S_{298}^\circ(H_2O(g)) - \Delta S_{298}^\circ(H_2O(l)) \\ &= 188.8\ \mathrm{J/K\cdot mol} - 70.0\ \mathrm{J/K\cdot mol} = 118.8\ \mathrm{J/K\cdot mol}\end{aligned}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3\ \mathrm{J/mol}}{118.8\ \mathrm{J/K\cdot mol}} = 370.5\ \mathrm{K} = 97.3\ ^\circ\mathrm{C}$$

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 (Tables T1 or T2.). 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 2.2.6.4

Use the information in Tables T1 or T2 to estimate the boiling point of CS_2.

Answer

313 K (accepted value 319 K).

Free Energy and Equilibrium

The free energy change for a process may be viewed as a measure of its driving force. A negative value for ΔG represents a driving force for the process in the forward direction, while a positive value represents a driving force for the process in the reverse direction. When ΔG is zero, the forward and reverse driving forces are equal, and the process occurs in both directions at the same rate (the system is at equilibrium).

In the chapter on equilibrium the *reaction quotient*, Q, was introduced as a convenient measure of the status of an equilibrium system. Recall that Q is the numerical value of the mass action expression for the system, and that you may use its value to identify the direction in which a reaction will proceed in order to achieve equilibrium. When Q is lesser than the equilibrium constant, K, the reaction will proceed in the forward direction until equilibrium is reached and $Q = K$. Conversely, if $Q > K$, the process will proceed in the reverse direction until equilibrium is achieved.

The free energy change for a process taking place with reactants and products present under *nonstandard conditions* (pressures other than 1 bar; concentrations other than 1 M) is related to the standard free energy change according to this equation:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

R is the gas constant (8.314 J/K mol), T is the kelvin or absolute temperature, and Q is the reaction quotient. For gas phase equilibria, the pressure-based reaction quotient, Q_P, is used. The concentration-based reaction quotient, Q_C, is used for condensed phase equilibria. This equation may be used to predict the spontaneity for a process under any given set of conditions as illustrated in Example 2.2.6.6.

✓ Example 2.2.6.6: Calculating ΔG under Nonstandard Conditions

What is the free energy change for the process shown here

$$2NH_3(g) \longrightarrow 3H_2(g) + N_2(g)$$

under the specified conditions?

- $T = 25°C$,
- $P_{N_2} = 0.870\text{ atm}$
- $P_{H_2} = 0.250\text{ atm}$
- $P_{NH_3} = 12.9\text{ atm}$

$$\Delta G^\circ = 33.0 kJ/mol$$

Solution

The equation relating free energy change to standard free energy change and reaction quotient may be used directly:

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT\ln Q \\ &= 33.0\frac{\text{kJ}}{\text{mol}} + \left(8.314\frac{\text{J}}{\text{mol K}} \times 298K \times \ln\frac{(0.250^3)\times 0.870}{12.9^2}\right) \\ &= 9680\frac{\text{J}}{\text{mol}}\text{ or } 9.68\text{ kJ/mol}\end{aligned}$$

Since the computed value for ΔG is positive, the reaction is nonspontaneous under these conditions.

? Exercise 2.2.6.6

Calculate the free energy change for this same reaction at 875 °C in a 5.00 L mixture containing 0.100 mol of each gas. Is the reaction spontaneous under these conditions?

Answer

ΔG = –123.5 kJ/mol; yes

For a system at equilibrium, $Q = K$ and $\Delta G = 0$, and the previous equation may be written as

$$0 = \Delta G^\circ + RT\ln K \quad \text{(at equilibrium)}$$

$$\Delta G^\circ = -RT\ln K$$

or

$$K = e^{-\frac{\Delta G}{RT}}$$

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in Table 2.2.6.2

Table 2.2.6.2: Relations between Standard Free Energy Changes and Equilibrium Constants

K	ΔG°	Composition of an Equilibrium Mixture
> 1	< 0	Products are more abundant
< 1	> 0	Reactants are more abundant
= 1	= 0	Reactants and products are comparably abundant

✓ Example 2.2.6.7: Calculating an Equilibrium Constant using Standard Free Energy Change

Given that the standard free energies of formation of $Ag^+(aq)$, $Cl^-(aq)$, and $AgCl(s)$ are 77.1 kJ/mol, −131.2 kJ/mol, and −109.8 kJ/mol, respectively, calculate the solubility product, K_{sp}, for AgCl.

Solution

The reaction of interest is the following:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = \left[Ag^+\right]\left[Cl^-\right]$$

The standard free energy change for this reaction is first computed using standard free energies of formation for its reactants and products:

$$\begin{aligned}\Delta G^\circ &= \left[\Delta G^\circ_f\left(\mathrm{Ag^+(aq)}\right) + \Delta G^\circ_f\left(\mathrm{Cl^-(aq)}\right)\right] - \left[\Delta G^\circ_f(\mathrm{AgCl(s)})\right] \\ &= [77.1\ \mathrm{kJ/mol} - 131.2\ \mathrm{kJ/mol}] - [-109.8\ \mathrm{kJ/mol}] = 55.7\ \mathrm{kJ/mol}\end{aligned}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change:

$$K_{sp} = e^{-\frac{\Delta G^\circ}{RT}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{55.7 \times 10^3 J/mol}{8.314 J/mol \cdot K \times 298.15 K}\right) = \exp(-22.470) = e^{-22.470} = 1.74 \times 10^{-10}$$

This result is in reasonable agreement with the value provided in Appendix J.

? Exercise 2.2.6.7

Use the thermodynamic data provided in Appendix G to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Answer

$K = 3.1$

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy 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 2.2.6.3). If a system consists of reactants and products in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

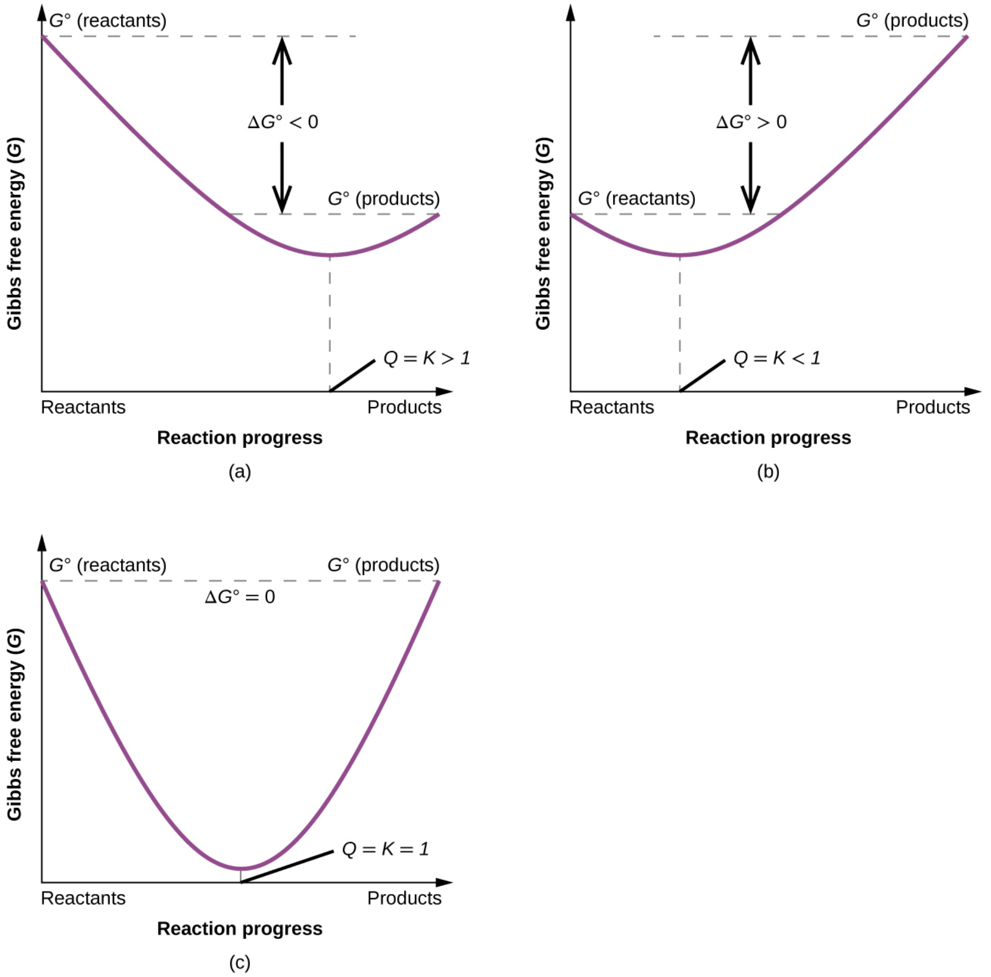


Figure 2.2.6.3: These plots show the free energy versus reaction progress for systems whose standard free energy changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium.

SECTION OVERVIEW

2.3: Kinetics

2.3.1: Chemical Reaction Rates

Learning Objectives

By the end of this section, you will be able to:

- 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.

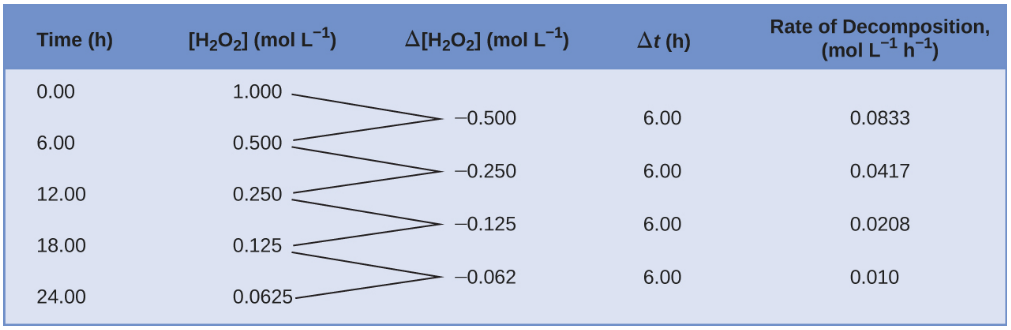
For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. For example, the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution changes slowly over time as it decomposes according to the equation:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l)+O_2(g)$$

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\begin{aligned} & H_2O_2 = -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ \text{rate of decomposition of} \quad & = -\frac{[H_2O_2]_{t_2}-[H_2O_2]_{t_1}}{t_2-t_1} \\ & = -\frac{\Delta\,[H_2O_2]}{\Delta t} \end{aligned}$$

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 t2; and Δ[H2O2] 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, $\Delta\,[\mathrm{H_2O_2}]$ is a negative quantity. Reaction rates are, by convention, positive quantities, and so this negative change in concentration is multiplied by −1. Figure 2.3.1.1 provides an example of data collected during the decomposition of $\mathrm{H_2O_2}$.



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 2.3.1.1: 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:

$$\frac{-\Delta [H_2O_2]}{\Delta t} = \frac{-(0.500 mol/L - 1.000 mol/L)}{(6.00 h - 0.00 h)} = 0.0833 mol L^{-1} h^{-1}$$

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:

$$\frac{-\Delta [H_2O_2]}{\Delta t} = \frac{-(0.0625 mol/L - 0.125 mol/L)}{(24.00 h - 18.00 h)} = 0.010 mol L^{-1} h^{-1}$$

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. In a plot of 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 $2.3.1.2$). These tangent line slopes may be evaluated using calculus, but the procedure for doing so is beyond the scope of this chapter.

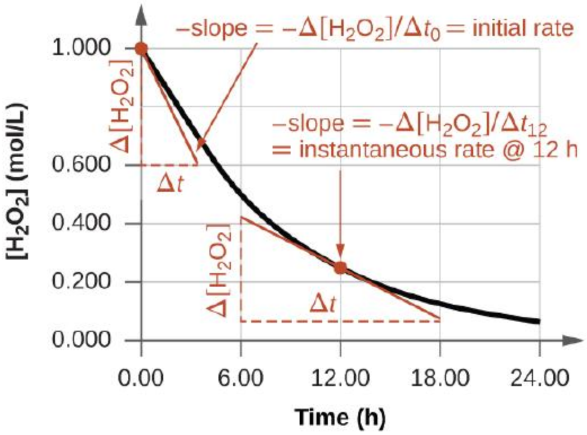


Figure $2.3.1.2$: This graph shows a plot of concentration versus time for a 1.000 *M* solution of H_2O_2. The rate at any time is equal to the negative of the slope of a line tangent to the curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 12 h ("instantaneous rate" at 12 h).

Chemistry in Everyday Life: 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 $2.3.1.3$). 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:

$$C_6H_{12}O_6 + O_2 \xrightarrow{\text{catalyst}} C_6H_{10}O_6 + H_2O_2$$

$$2H_2O_2 + 2I^- \xrightarrow{\text{catalyst}} I_2 + 2H_2O + O_2$$

The first equation 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, 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.

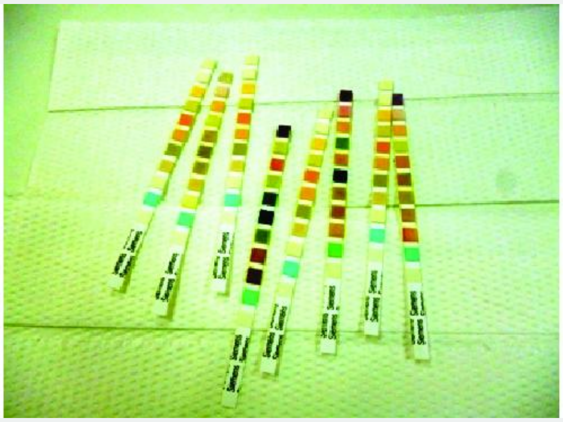


Figure 2.3.1.3: Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman)

Relative Rates of Reaction

The rate of a reaction may be expressed as the change in concentration of any reactant or product. For any given reaction, these rate expressions are all related simply to one another according to the reaction stoichiometry. The rate of the general reaction

$$A \longrightarrow B \tag{2.3.1.1}$$

can be expressed in terms of the decrease in the concentration of A or the increase in the concentration of B. These two rate expressions are related by the stoichiometry of the reaction:

$$\text{rate } = -\left(\frac{1}{a}\right)\left(\frac{\Delta A}{\Delta t}\right) = \left(\frac{1}{b}\right)\left(\frac{\Delta B}{\Delta t}\right)$$

Consider the reaction represented by the following equation:

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$$

The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta mol\ NH_3}{\Delta t} \times \frac{1 mol\ N_2}{2 mol\ NH_3} = \frac{\Delta mol\ N_2}{\Delta t}$$

This may be represented in an abbreviated format by omitting the units of the stoichiometric factor:

$$-\frac{1}{2}\frac{\Delta mol\ NH_3}{\Delta t} = \frac{\Delta mol\ N_2}{\Delta t}$$

Note that a negative sign has been included as a factor to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). For homogeneous reactions, both the reactants and products are present in the same solution and thus occupy the same volume, so the molar amounts may be replaced with molar concentrations:

$$-\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}=\frac{\Delta[N_2]}{\Delta t}$$

Similarly, the rate of formation of H_2 is three times the rate of formation of N_2 because three moles of H_2 are produced for each mole of N_2 produced.

$$\frac{1}{3}\frac{\Delta[H_2]}{\Delta t}=\frac{\Delta[N_2]}{\Delta t}$$

Figure 2.3.1.4 illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. Slopes of the tangent lines at *t* = 500 s show that the instantaneous rates derived from all three species involved in the reaction 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:

$$\frac{2.91\times10^{-6}\,M/s}{9.70\times10^{-7}\,M/s}\approx 3$$

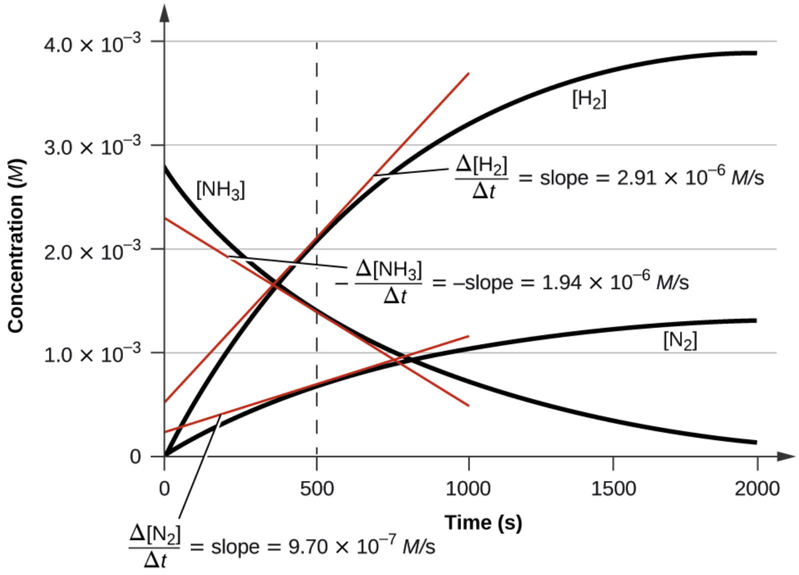


Figure 2.3.1.4: Changes in concentrations of the reactant and products for the reaction $2\,NH_3 \longrightarrow N_2 + 3\,H_2$. The rates of change of the three concentrations are related by the reaction stoichiometry, as shown by the different slopes of the tangents at *t* = 500 s.

✓ Example 2.3.1.1: Expressions for Relative Reaction Rates

The first step in the production of nitric acid is the combustion of ammonia:

$$4NH_3(g)+5O_2(g)\longrightarrow 4NO(g)+6H_2O(g) \tag{2.3.1.2}$$

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:

$$-\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t}=-\frac{1}{5}\frac{\Delta[O_2]}{\Delta t}=\frac{1}{4}\frac{\Delta[NO]}{\Delta t}=\frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

Exercise 2.3.1.1

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:

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Answer

$$-\frac{1}{5}\frac{\Delta\left[Br^-\right]}{\Delta t} = -\frac{\Delta\left[BrO_3^-\right]}{\Delta t} = -\frac{1}{6}\frac{\Delta\left[H^+\right]}{\Delta t} = \frac{1}{3}\frac{\Delta\left[Br_2\right]}{\Delta t} = \frac{1}{3}\frac{\Delta\left[H_2O\right]}{\Delta t}$$

Example 2.3.1.2: Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure 2.3.1.2 shows the rate of the decomposition of H_2O_2 over time:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

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:

$$-\frac{1}{2}\frac{\Delta\left[\mathrm{H_2O_2}\right]}{\Delta t} = \frac{1}{2}\frac{\Delta\left[\mathrm{H_2O}\right]}{\Delta t} = \frac{\Delta\left[\mathrm{O_2}\right]}{\Delta t} \tag{2.3.1.3}$$

What is the instantaneous rate of production of H_2O and O_2?

Solution

The reaction stoichiometry shows that

$$-\frac{1}{2}\frac{\Delta\left[\mathrm{H_2O_2}\right]}{\Delta t} = \frac{1}{2}\frac{\Delta\left[\mathrm{H_2O}\right]}{\Delta t} = \frac{\Delta\left[\mathrm{O_2}\right]}{\Delta t} \tag{2.3.1.4}$$

Therefore:

$$\frac{1}{2} \times 3.20 \times 10^{-2} mol L^{-1} h^{-1} = \frac{\Delta\left[O_2\right]}{\Delta t}$$

and

$$\frac{\Delta\left[O_2\right]}{\Delta t} = 1.60 \times 10^{-2} mol L^{-1} h^{-1}$$

Exercise 2.3.1.2

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.

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2.3.2: Factors Affecting Reaction Rates

Learning Objectives

By the end of this section, you will be able to:

- 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. Five factors typically affecting the rates of chemical reactions will be explored in this section: 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.

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.

The Physical States of the Reactants

A chemical reaction between two or more substances requires intimate contact between the reactants. When reactants are in different physical states, or phases (solid, liquid, gaseous, dissolved), the reaction takes place only at the interface between the phases. Consider the heterogeneous reaction between a solid phase and either a liquid or gaseous phase. Compared with the reaction rate for large solid particles, the rate for smaller particles will be greater because the surface area in contact with the other reactant phase is greater. For example, large pieces of iron react more slowly with acids than they do with finely divided iron powder (Figure 2.3.2.1). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.

(a)

(b)

Figure 2.3.2.1: (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas: $2Fe(s) + 6HCl(aq)\ 2FeCl_3(aq) + 3H_2(g)$. (b) An iron nail reacts more slowly because the surface area exposed to the acid is much less.

Link to Learning

Watch this video to see the reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.

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. Gas burners, hot plates, and ovens are often used in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. For many chemical processes, reaction rates are approximately doubled when the temperature is raised by 10 °C.

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 2.3.2.2). An acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$\mathrm{SO_2(g) + H_2O(g) \longrightarrow H_2SO_3(aq)}$$

Calcium carbonate reacts with sulfurous acid as follows:

$$\mathrm{CaCO_3(s) + H_2SO_3(aq) \longrightarrow CaSO_3(aq) + CO_2(g) + H_2O(l)}$$

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 2.3.2.2: 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)

Link to Learning

Phosphorus burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen is higher. Watch this video to see an example.

The Presence of a Catalyst

Relatively dilute aqueous solutions of hydrogen peroxide, H_2O_2, are commonly used as topical antiseptics. Hydrogen peroxide decomposes to yield water and oxygen gas according to the equation:

$$\mathrm{2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g)}$$

Under typical conditions, this decomposition occurs very slowly. When dilute $H_2O_2(aq)$ is poured onto an open wound, however, the reaction occurs rapidly and the solution foams because of the vigorous production of oxygen gas. This dramatic difference is caused by the presence of substances within the wound's exposed tissues that accelerate the decomposition process. Substances that function to increase the rate of a reaction are called **catalysts**, a topic treated in greater detail later in this chapter.

Link to Learning

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.

2.3.3: Rate Laws

Learning Objectives

By the end of this section, you will be able to:

- 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 often affected by the concentrations of reactants. Rate laws (sometimes called *differential 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. As an example, consider the reaction described by the chemical equation

$$aA + bB \longrightarrow \text{ products}$$

where a and b are stoichiometric coefficients. The rate law for this reaction is written as:

$$\text{rate } = k[A]^m[B]^n$$

in which [*A*] and [*B*] 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* and *n* are the **reaction orders** and are typically positive integers, though they can be fractions, negative, or zero. The rate constant *k* and the reaction orders *m* and *n* 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 reactant concentrations, but it does vary with temperature.

The reaction orders in a rate law describe the mathematical dependence of the rate on reactant concentrations. Referring to the generic rate law above, the reaction is *m* order with respect to *A* and *n* order with respect to *B*. For example, if *m* = 1 and *n* = 2, the reaction is first order in *A* and second order in *B*. The overall reaction order is simply the sum of orders for each reactant. For the example rate law here, the reaction is third order overall (1 + 2 = 3). A few specific examples are shown below to further illustrate this concept.

The rate law:

$$\text{rate } = k\left[H_2O_2\right]$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate } = k\left[\mathrm{C_4H_6}\right]^2$$

describes a reaction that is second order in $\mathrm{C_4H_6}$ and second order overall. The rate law:

$$\text{rate } = k\left[\mathrm{H^+}\right]\left[\mathrm{OH^-}\right]$$

describes a reaction that is first order in $\mathrm{H^+}$, first order in $\mathrm{OH^-}$, and second order overall.

Example 2.3.3.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\mathrm{NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)}$$

is second order in $\mathrm{NO_2}$ and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate } = k[\mathrm{NO_2}]^m[\mathrm{CO}]^n$$

The reaction is second order in $\mathrm{NO_2}$; thus $m = 2$. The reaction is zero order in CO; thus $n = 0$. The rate law is:

$$\text{rate } = k[\mathrm{NO_2}]^2[\mathrm{CO}]^0 = k[\mathrm{NO_2}]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[\mathrm{CO}]^0 = 1$, which is why the CO concentration term may be omitted from the rate law: the rate of reaction is solely dependent on the concentration of $\mathrm{NO_2}$. A later chapter section on reaction mechanisms will explain how a reactant's concentration can have no effect on a reaction rate despite being involved in the reaction.

? Exercise $2.3.3.1A$

The rate law for the reaction:

$$\mathrm{H_2(g) + 2\,NO(g) \longrightarrow N_2O(g) + H_2O(g)}$$

has been determined to be rate = $k[\mathrm{NO}]^2[\mathrm{H_2}]$. 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 $2.3.3.1B$

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol $(\mathrm{CH_3OH})$ and ethyl acetate $(\mathrm{CH_3CH_2OCOCH_3})$ as a sample reaction before studying the chemical reactions that produce biodiesel:

$$\mathrm{CH_3OH + CH_3CH_2OCOCH_3 \longrightarrow CH_3OCOCH_3 + CH_3CH_2OH}$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, determined to be:

$$\text{rate } = k\left[\mathrm{CH_3OH}\right]$$

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

A common experimental approach to the determination of rate laws is the **method of initial rates**. This method involves measuring reaction rates for multiple experimental trials carried out using different initial reactant concentrations. Comparing the measured rates for these trials permits determination of the reaction orders and, subsequently, the rate constant, which together are used to formulate a rate law. This approach is illustrated in the next two example exercises.

✓ Example 2.3.3.2: 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 $2.3.3.1$). One such reaction is the combination of nitric oxide, NO, with ozone, O_3:

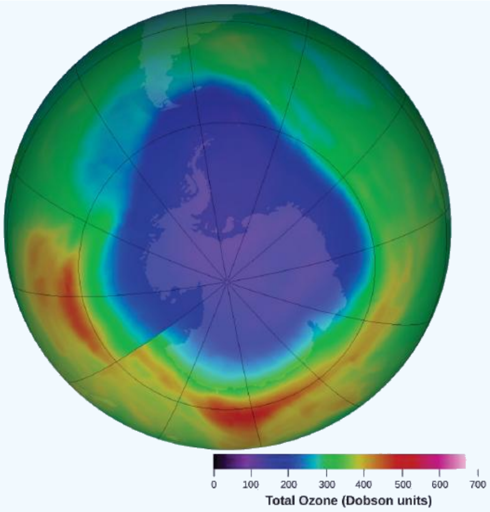


Figure 2.3.3.1: A contour map showing stratospheric ozone concentration and the “ozone hole” that occurs over Antarctica during its spring months. (credit: modification of work by NASA)

$$\mathrm{NO(g)} + \mathrm{O_3(g)} \longrightarrow \mathrm{NO_2(g)} + \mathrm{O_2(g)}$$

This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	[NO] (mol/L)	[O_3] (mol/L)	$\frac{\Delta[\mathrm{NO_2}]}{\Delta t}(\mathrm{molL^{-1}s^{-1}})$
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:

$$\text{rate } = k[NO]^m[O_3]^n$$

Determine the values of *m*, *n*, and *k* from the experimental data using the following three-part process:

Step 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.

Step 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:

$$\text{rate } = k[NO]^1[O_3]^1 = k[NO]\,[O_3]$$

Step 3:

Determine the value of k *from one set of concentrations and the corresponding rate*. The data from trial 1 are used below:

$$
\begin{aligned}
k &= \frac{\text{rate}}{[\text{NO}]\,[\text{O}_3]} \\
&= \frac{6.60\times10^{-5}\ \text{mol L}^{-1}\text{s}^{-1}}{\left(1.00\times10^{-6}\ \text{mol L}^{-1}\right)\left(3.00\times10^{-6}\ \text{mol L}^{-1}\right)} \\
&= 2.20\times10^{7}\ \text{L mol}^{-1}\text{s}^{-1}
\end{aligned}
$$

Exercise 2.3.3.2

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

$$\text{CH}_3\text{CHO(g)} \longrightarrow \text{CH}_4\text{(g)} + \text{CO(g)}$$

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

rate $= k[\text{CH}_3\text{CHO}]^2$ with $k = 6.7310^{-6}$ L/mol/s

Example 2.3.3.3: 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:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

Trial	[NO] (mol/L)	$[\text{Cl}_2]$ (mol/L)	$-\frac{\Delta[\text{CO}]}{\Delta t}(\text{mol } L^{-1}\text{s}^{-1})$
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:

$$\text{rate } = k[NO]^m[Cl_2]^n$$

As in Example 2.3.3.2, 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, an explicit algebraic approach (vs. the implicit approach of the previous example) will be used to determine the values of *m* and *n*:

Step 1

Determine the value of m from the data in which $[\text{NO}]$ varies and $[\text{Cl}_2]$ is constant. Write the ratios with the subscripts x and y to indicate data from two different trials:

$$\frac{\text{rate }_x}{\text{rate }_y} = \frac{k[NO]_x^m[Cl_2]_x^n}{k[NO]_y^m[Cl_2]_y^n}$$

Using the third trial and the first trial, in which $[\mathrm{Cl_2}]$ does not vary, gives:

$$\frac{\text{rate 3}}{\text{rate 1}}=\frac{0.00675}{0.00300}=\frac{k(0.15)^m(0.10)^n}{k(0.10)^m(0.10)^n}$$

Canceling equivalent terms in the numerator and denominator leaves:

$$\frac{0.00675}{0.00300}=\frac{(0.15)^m}{(0.10)^m}$$

which simplifies to:

$$2.25=(1.5)^m$$

Use logarithms to determine the value of the exponent *m*:

$$\ln(2.25)=m\ln(1.5)$$

$$\frac{\ln(2.25)}{\ln(1.5)}=m$$

$$2=m$$

Confirm the result

$$1.5^2=2.25$$

Step 2

Determine the value of n from data in which $[\mathrm{Cl_2}]$ varies and $[\mathrm{NO}]$ is constant.

$$\frac{\text{rate 2}}{\text{rate 1}}=\frac{0.00450}{0.00300}=\frac{k0.10)^m(0.15)^n}{k(0.10)^m(0.10)^n}$$

Cancelation gives:

$$\frac{0.0045}{0.0030}=\frac{(0.15)^n}{(0.10)^n}$$

which simplifies to:

$$1.5=(1.5)^n$$

Thus n must be 1, and the form of the rate law is:

$$\text{rate }=k[NO]^m[Cl_2]^n=k[NO]^2\,[Cl_2]$$

Step 3.

Determine the numerical value of the constant with appropriate units. The units for the rate of a reaction are mol/L/s. The units for 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 mol$^-$ L/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*:

$$0.00300\ \mathrm{mol\ L^{-1}s^{-1}}=k\left(0.10\ \mathrm{mol\ L^{-1}}\right)^2\left(0.10\ \mathrm{mol\ L^{-1}}\right)^1$$

$$k=3.0\ \mathrm{mol^{-2}L^2s^{-1}}$$

Exercise 2.3.3.3

Use the provided initial rate data to derive the rate law for the reaction whose equation is:

$$\mathrm{OCl^-(aq) + I^-(aq) \longrightarrow OI^-(aq) + Cl^-(aq)}$$

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

$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{0.00092}{0.00046} = \frac{k(0.0020)^x(0.0040)^y}{k(0.0020)^x(0.0020)^y}$$

$$2.00 = 2.00^y$$

$$y = 1$$

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{0.00184}{0.00092} = \frac{k(0.0040)^x(0.0020)^y}{k(0.0020)^x(0.0040)^y}$$

$$2.00 = \frac{2^x}{2^y}$$

$$2.00 = \frac{2^x}{2^1}$$

$$4.00 = 2^x$$

$$x = 2$$

Substituting the concentration data from trial 1 and solving for k yields:

$$\begin{aligned} \text{rate } &= k\left[OCl^-\right]^2\left[I^-\right]^1 \\ 0.00184 &= k(0.0040)^2(0.0020)^1 \\ k &= 5.75 \times 10^4 mol^{-2}L^2s^{-1} \end{aligned}$$

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:

$$\begin{aligned} \mathrm{NO_2 + CO} &\longrightarrow \mathrm{NO + CO_2} & \text{rate } &= k[NO_2]^2 \\ \mathrm{CH_3CHO} &\longrightarrow \mathrm{CH_4 + CO} & \text{rate } &= k[CH_3CHO]^2 \\ \mathrm{2\,N_2O_5} &\longrightarrow \mathrm{NO_2 + O_2} & \text{rate } &= k\,[N_2O_5] \\ \mathrm{2\,NO_2 + F_2} &\longrightarrow \mathrm{2\,NO_2F} & \text{rate } &= k\,[NO_2]\,[F_2] \\ \mathrm{2\,NO_2Cl} &\longrightarrow \mathrm{2\,NO_2 + Cl_2} & \text{rate } &= k\,[NO_2Cl] \end{aligned}$$

Note

It is important to note that *rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

The units for a rate constant will vary as appropriate to accommodate the overall order of the reaction. The unit of the rate constant for the second-order reaction described in Example $2.3.3.2$was determined to be k was derived to be $\mathrm{L\,mol^{-1}s^{-1}}$. For the third-order reaction, k was derived to be $\mathrm{L^2mol^{-2}s^{-1}}$. Dimensional analysis requires the rate constant unit for a reaction whose overall order is x to be $\mathrm{L}^{x-1}\ \mathrm{mol}^{1-x}\mathrm{s}^{-1}$. Table $2.3.3.1$summarizes the rate constant units for common reaction orders.

Table $2.3.3.1$: Rate Constant Units for Common Reaction Orders

Overall Reaction Order (x)	Rate Constant Unit ($\mathrm{L}^{x-1}\ \mathrm{mol}^{1-x}\ \mathrm{s}^{-1}$)
0 (zero)	$\mathrm{mol\ L^{-1}\ s^{-1}}$
1 (first)	$\mathrm{s^{-1}}$
2 (second)	$\mathrm{L\ mol^{-1}\ s^{-1}}$
3 (third)	$\mathrm{L^2\ mol^{-2}\ s^{-1}}$

Note that the units in this table were derived using specific units for concentration (mol/L) and time (s), though any valid units for these two properties may be used.

2.3.4: Integrated Rate Laws

Learning Objectives

By the end of this section, you will be able to:

- 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 discussed 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.

First-Order Reactions

Integration of the rate law for a simple first-order reaction (rate = $k[A]$) results in an equation describing how the reactant concentration varies with time:

$$[A]_t = [A]_0 e^{-kt}$$

where $[A]t$ is the concentration of A at any time t, $[A]_0$ is the initial concentration of A, and k is the first-order rate constant.

For mathematical convenience, this equation may be rearranged to other formats, including direct and indirect proportionalities:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

or

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

and a format showing a linear dependence of concentration in time:

$$\ln[A]_t = \ln[A]_0 - kt$$

✓ Example 2.3.4.1: 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 10^{-3} s^{-1}:

$$C_4H_8 \longrightarrow 2\,C_2H_4$$

How long will it take for 80.0% of a sample of C_4H_8 to decompose?

Solution

Since the relative change in reactant concentration is provided, a convenient format for the integrated rate law is:

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

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:

$$\begin{aligned} t &= \ln \frac{[x]}{[0.200x]} \times \frac{1}{k} \\ &= \ln 5 \times \frac{1}{9.2 \times 10^{-3}\ \mathrm{s}^{-1}} \\ &= 1.609 \times \frac{1}{9.2 \times 10^{-3}\ \mathrm{s}^{-1}} \\ &= 1.7 \times 10^{2}\ \mathrm{s} \end{aligned}$$

? Exercise 2.3.4.1

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:

$$\text{I-131} \longrightarrow \text{Xe-131} + \text{electron}$$

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

In the next example exercise, a linear format for the integrated rate law will be convenient:

$$\ln[A]_t = (-k)(t) + \ln[A]_0$$
$$y = mx + b$$

A plot of $\ln[A]_t$ versus t for a first-order reaction is a straight line with a slope of $-k$ and a y-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 2.3.4.2: Graphical Determination of Reaction Order and Rate Constant

Show that the data in Figure 2.3.4.1can be represented by a first-order rate law by graphing $\ln[H_2O_2]$ versus time. Determine the rate constant for the decomposition of H_2O_2 from these data.

Solution

The data from Figure 2.3.4.1are tabulated below, and a plot of $\ln[H_2O_2]$ is shown in Figure 2.3.4.1

Time (h)	$[H_2O_2]$ (*M*)	$\ln[H_2O_2]$
0.00	1.000	0.000
6.00	0.500	−0.693
12.00	0.250	−1.386
18.00	0.125	−2.079
24.00	0.0625	−2.772

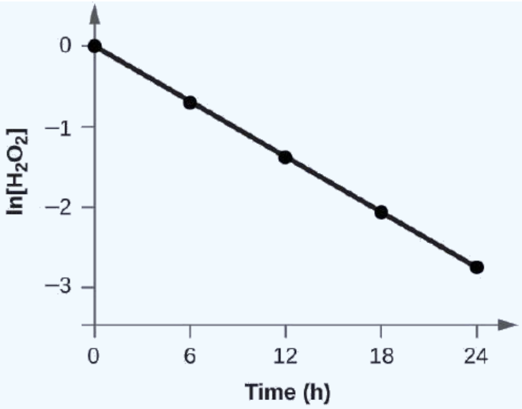


Figure 2.3.4.1: A linear relationship between $\ln[H_2O_2]$ and time suggests the decomposition of hydrogen peroxide is a first-order reaction.

The plot of $\ln[H_2O_2]$ versus time is linear, indicating that the reaction may be described by a first-order rate law.

According to the linear format of the first-order integrated rate law, the rate constant is given by the negative of this plot's slope.

$$\text{slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln[H_2O_2]}{\Delta t}$$

The slope of this line may be derived from 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 0.00 h is 0.000; the value when *t* = 24.00 h is −2.772

$$\begin{aligned}\text{slope} &= \frac{-2.772 - 0.000}{24.00 - 0.00h} \\ &= \frac{-2.772}{24.00h} \\ &= -0.116h^{-1} \\ k &= -\text{slope} = -\left(-0.116h^{-1}\right) = 0.116h^{-1}\end{aligned}$$

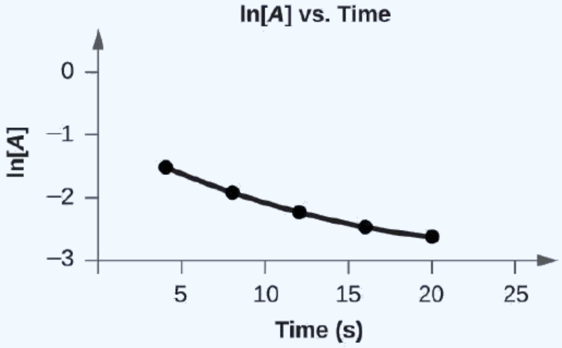
? Exercise 2.3.4.2

Graph the following data to determine whether the reaction $A \longrightarrow B + C$ is first order.

Time (s)	[*A*]
4.0	0.220
8.0	0.144
12.0	0.110
16.0	0.088
20.0	0.074

Answer

The plot of $\ln[A]_t$ vs. *t* is not linear, indicating the reaction is not first order:



Second-Order Reactions

The equations that relate the concentrations of reactants and the rate constant of second-order reactions can be fairly complicated. To illustrate the point with minimal complexity, only the simplest second-order reactions will be described here, namely, those whose rates depend on the concentration of just one reactant. For these types of reactions, the differential rate law is written as:

$$\text{rate } = k[A]^2$$

For these second-order reactions, the integrated rate law is:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

where the terms in the equation have their usual meanings as defined earlier.

✓ Example 2.3.4.3: The Integrated Rate Law for a Second-Order Reaction

The reaction of butadiene gas (C_4H_6) to yield C_8H_{12} gas is described by the equation:

$$2C_4H_6(g) \longrightarrow C_8H_{12}(g)$$

This “dimerization” reaction is second order with a rate constant equal to 5.76 10^{-2} L mol^{-1} min^{-1} under certain conditions. If the initial concentration of butadiene is 0.200 *M*, what is the concentration after 10.0 min?

Solution

For a second-order reaction, the integrated rate law is written

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

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:

$$\begin{aligned}\frac{1}{[A]_t} &= \left(5.76 \times 10^{-2} Lmol^{-1}min^{-1}\right)(10min) + \frac{1}{0.200mol^{-1}} \\ &= \left(5.76 \times 10^{-1} Lmol^{-1}\right) + 5.00 Lmol^{-1} \\ &= 5.58 Lmol^{-1} \\ [A]_t &= 1.79 \times 10^{-1} molL^{-1}\end{aligned}$$

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 2.3.4.3

If the initial concentration of butadiene is 0.0200 *M*, what is the concentration remaining after 20.0 min?

Answer

0.0195 mol/L

The integrated rate law for second-order reactions has the form of the equation of a straight line:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$y = mx + b$$

A plot of $\frac{1}{[A]_t}$ versus t for a second-order reaction is a straight line with a slope of k and a y-intercept of $\frac{1}{[A]_0}$. If the plot is not a straight line, then the reaction is not second order.

✓ Example 2.3.4.4: Graphical Determination of Reaction Order and Rate Constant

The data below are for the same reaction described in Example $2.3.4.3$. Prepare and compare two appropriate data plots to identify the reaction as being either first or second order. After identifying the reaction order, estimate a value for the rate constant.

Solution

Time (s)	$[C_4H_6]$ (M)
0	1.00×10^{-2}
1600	5.04×10^{-3}
3200	3.37×10^{-3}
4800	2.53×10^{-3}
6200	2.08×10^{-3}

In order to distinguish a first-order reaction from a second-order reaction, prepare a plot of $\ln[C_4H_6]_t$ versus t and compare it to a plot of $\frac{1}{[C_4H_6]_t}$ 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 $2.3.4.2$, which clearly shows the plot of $\ln[C_4H_6]_t$ versus t is not linear, therefore the reaction is not first order. The plot of $\frac{1}{[C_4H_6]_t}$ versus t is linear, indicating that the reaction is second order.

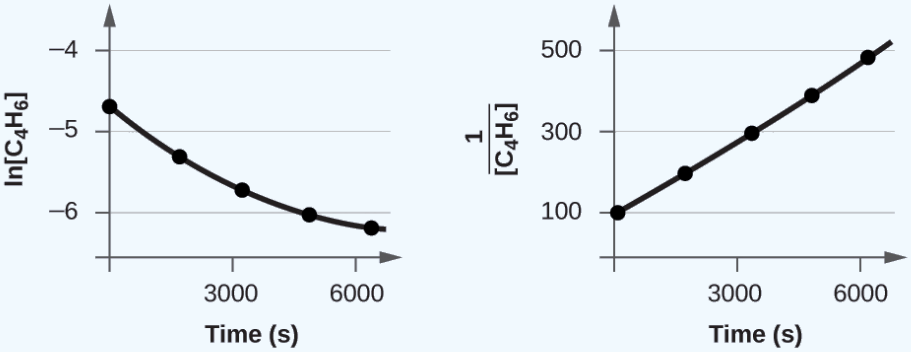


Figure 2.3.4.2: These two graphs show first- and second-order plots for the dimerization of C_4H_6. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

According to the second-order integrated rate law, the rate constant is equal to the slope of the versus *t* plot. Using the data for *t* = 0 *s* and *t* = 6200 *s*, the rate constant is estimated as follows:

$$k = \text{slope } = \frac{\left(481M^{-1} - 100M^{-1}\right)}{(6200s - 0s)} = 0.0614M^{-1}s^{-1}$$

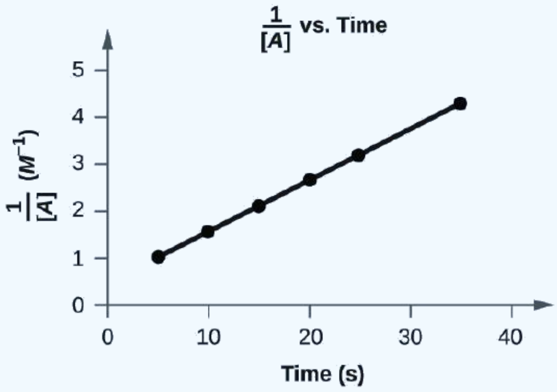
? Exercise 2.3.4.4

Do the following data fit a second-order rate law?

Time (s)	[*A*] (*M*)
5	0.952
10	0.625
15	0.465
20	0.370
25	0.308
35	0.230

Answer

Yes. The plot of $\frac{1}{[A]_t}$ vs. t is linear:



Zero-Order Reactions

For zero-order reactions, the differential rate law is:

$$\text{rate } = k$$

A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactant(s). This may seem counterintuitive, since the reaction rate certainly can't be finite when the reactant concentration is zero. For purposes of this introductory text, it will suffice to note that zero-order kinetics are observed for some reactions only under certain specific conditions. These same reactions exhibit different kinetic behaviors when the specific conditions aren't met, and for this reason the more prudent term *pseudo-zero-order* is sometimes used.

The integrated rate law for a zero-order reaction is a linear function:

$$[A]_t = -kt + [A]_0$$

$$y = mx + b$$

A plot of [*A*] versus *t* for a zero-order reaction is a straight line with a slope of −*k* and a *y*-intercept of $[A]_0$. Figure 2.3.4.3 shows a plot of $[NH_3]$ versus *t* for the thermal decomposition of ammonia at the surface of two different heated solids. The decomposition reaction exhibits first-order behavior at a quartz (SiO_2) surface, as suggested by the exponentially decaying plot of concentration versus time. On a tungsten surface, however, the plot is linear, indicating zero-order kinetics.

✓ Example 2.3.4.5: Graphical Determination of Zero-Order Rate Constant

Use the data plot in Figure 2.3.4.3 to graphically estimate the zero-order rate constant for ammonia decomposition at a tungsten surface.

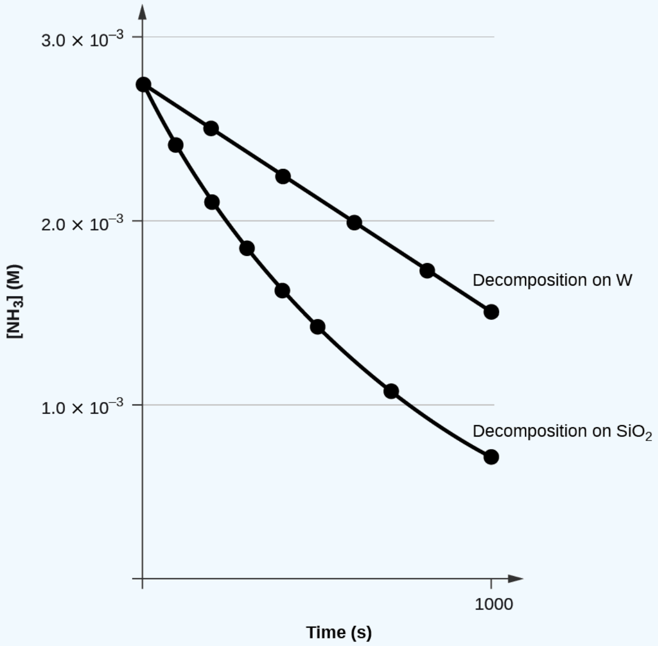


Figure 2.3.4.3: The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.

Solution

The integrated rate law for zero-order kinetics describes a linear plot of reactant concentration, $[A]_t$, versus time, t, with a slope equal to the negative of the rate constant, $-k$. Following the mathematical approach of previous examples, the slope of the linear data plot (for decomposition on W) is estimated from the graph. Using the ammonia concentrations at $t = 0$ and $t = 1000$ s:

$$k = -\text{ slope } = -\frac{\left(0.0015 mol L^{-1} - 0.0028 mol L^{-1}\right)}{(1000 s - 0 s)} = 1.3 \times 10^{-6} mol L^{-1} s^{-1}$$

? Exercise 2.3.4.5

The zero-order plot in Figure 2.3.4.3 shows an initial ammonia concentration of 0.0028 mol L^{-1} decreasing linearly with time for 1000 s. Assuming no change in this zero-order behavior, at what time (min) will the concentration reach 0.0001 mol L^{-1}?

Answer

35 min

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 (Figure 2.3.4.1) 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.

First-Order Reactions

An equation relating the half-life of a first-order reaction to its rate constant may be derived from the integrated rate law as follows:

$$\ln \frac{[A]_0}{[A]_t} = kt$$

$$t = \ln \frac{[A]_0}{[A]_t} \times \frac{1}{k}$$

Invoking the definition of half-life, symbolized requires that the concentration of *A* at this point is one-half its initial concentration: $t = t_{1/2}$, $[A]_t = \frac{1}{2}[A]_0$

Substituting these terms into the rearranged integrated rate law and simplifying yields the equation for half-life:

$$\begin{aligned} t_{1/2} &= \ln \frac{[A]_0}{\frac{1}{2}[A]_0} \times \frac{1}{k} \\ &= \ln 2 \times \frac{1}{k} = 0.693 \times \frac{1}{k} \\ t_{1/2} &= \frac{0.693}{k} \end{aligned}$$

This equation describes an expected inverse relation between the half-life of the reaction and its rate constant, *k*. Faster reactions exhibit larger rate constants and correspondingly shorter half-lives. Slower reactions exhibit smaller rate constants and longer half-lives.

✓ Example 2.3.4.6: 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 2.3.4.4

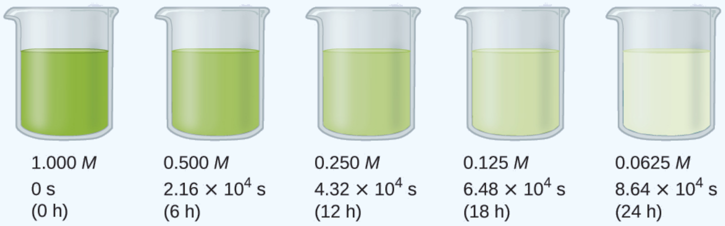


Figure 2.3.4.4: The decomposition of H_2O_2 at 40 °C is illustrated. The intensity of the color symbolizes the concentration of H_2O_2 at the indicated times; H_2O_2 is actually colorless.

Solution

Inspecting the concentration/time data in Figure 2.3.4.4shows the half-life for the decomposition of H_2O_2 is 2.16×10^4 s:

$$\begin{aligned} t_{1/2} &= \frac{0.693}{k} \\ k &= \frac{0.693}{t_{1/2}} = \frac{0.693}{2.16 \times 10^4 s} = 3.21 \times 10^{-5} s^{-1} \end{aligned}$$

? Exercise 2.3.4.1

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.

Second-Order Reactions

Following the same approach as used for first-order reactions, an equation relating the half-life of a second-order reaction to its rate constant and initial concentration may be derived from its integrated rate law:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

or

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

Restrict t to $t_{1/2}$

$$t = t_{1/2}$$

define $[A]_t$ as one-half $[A]_0$

$$[A]_t = \frac{1}{2}[A]_0$$

and then substitute into the integrated rate law and simplify:

$$\begin{aligned} \frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} &= kt_{1/2} \\ \frac{2}{[A]_0} - \frac{1}{[A]_0} &= kt_{1/2} \\ \frac{1}{[A]_0} &= kt_{1/2} \\ t_{1/2} &= \frac{1}{k[A]_0} \end{aligned}$$

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. 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.

Zero-Order Reactions

As for other reaction orders, an equation for zero-order half-life may be derived from the integrated rate law:

$$[A] = -kt + [A]_0$$

Restricting the time and concentrations to those defined by half-life: and Substituting these terms into the zero-order integrated rate law yields:

$$\begin{aligned} \frac{[A]_0}{2} &= -kt_{1/2} + [A]_0 \\ kt_{1/2} &= \frac{[A]_0}{2} \\ t_{1/2} &= \frac{[A]_0}{2k} \end{aligned}$$

As for all reaction orders, the half-life for a zero-order reaction is inversely proportional to its rate constant. However, 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 $2.3.4.1$.

Table $2.3.4.1$: 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	vs. t
relationship between slope of linear plot and rate constant	$k = -$slope	$k = -$slope	$k =$ slope
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

✓ Example $2.3.4.7$: Half-Life for Zero-Order and Second-Order Reactions

What is the half-life for the butadiene dimerization reaction described in Example $2.3.4.3$?

Solution

The reaction in question is second order, is initiated with a 0.200 mol L^{-1} reactant solution, and exhibits a rate constant of 0.0576 L mol^{-1} min^{-1}. Substituting these quantities into the second-order half-life equation:

$$t_{1/2} = \frac{1}{[(0.0576 Lmol^{-1} min^{-1})(0.200 molL^{-1})]} = 86.8 \text{ min}$$

? Exercise $2.3.4.7$

What is the half-life (min) for the thermal decomposition of ammonia on tungsten (see Figure $2.3.4.3$)?

Answer

87 min

2.3.5: Collision Theory

Learning Objectives

By the end of this section, you will be able to:

- 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:

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:

$$2\,\mathrm{CO}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CO_2}(g)$$

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 amounts, the reaction will occur 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:

$$\mathrm{CO}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{O}(g)$$

Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in Figure $2.3.5.1$. 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 (\ce{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.

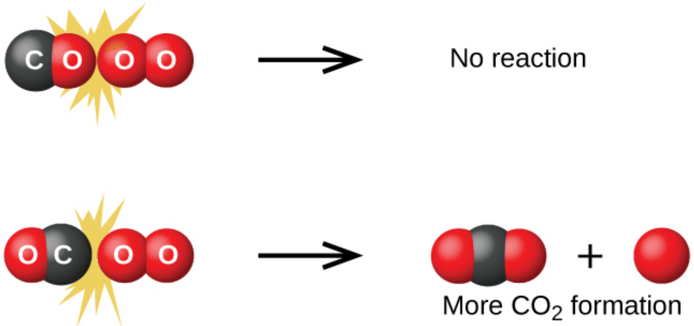


Figure 2.3.5.1: Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. In addition to a proper orientation, the collision must also occur with sufficient energy to result in product formation. When reactant species collide with both proper orientation and adequate energy, they combine to form an unstable species called an **activated complex** or a **transition state**. These species are very short lived and usually undetectable by most analytical instruments. In some cases, sophisticated spectral measurements have been used to observe transition states.

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.

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). How this energy compares to the kinetic energy provided by colliding reactant molecules is a primary factor affecting the rate of a chemical reaction. If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly since 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, a large fraction of molecules will be adequately energetic and the reaction will proceed rapidly.

Figure 2.3.5.2 shows how the energy of a chemical system changes as it undergoes a reaction converting reactants to products according to the equation

$$\mathrm{A^{+}B \longrightarrow C^{+}D}$$

These reaction diagrams are widely used in chemical kinetics to illustrate various properties of the reaction of interest. Viewing the diagram from left to right, the system initially comprises reactants only, $\mathrm{A+B}$. Reactant molecules with sufficient energy can collide to form a high-energy activated complex or transition state. The unstable transition state can then subsequently decay to yield stable products, $C + D$. The diagram depicts the reaction's activation energy, E_a, as the energy difference between the reactants and the transition state. Using a specific energy, the *enthalpy* (see chapter on thermochemistry), the enthalpy change of the reaction, ΔH, is estimated as the energy difference between the reactants and products. In this case, the reaction is exothermic ($\Delta H < 0$) since it yields a decrease in system enthalpy.

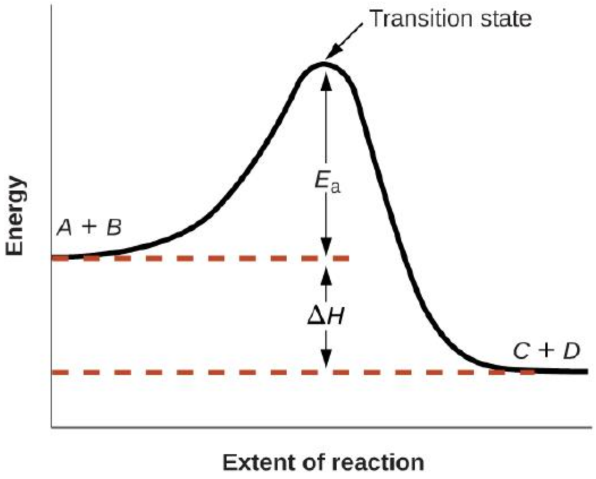


Figure 2.3.5.2: Reaction diagram for the exothermic reaction

The **Arrhenius equation** relates the activation energy and the rate constant, *k*, for many chemical reactions:

$$k = Ae^{-E_a/RT}$$

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.

Postulates of collision theory are nicely accommodated by the Arrhenius equation. The frequency factor, *A*, reflects how well the reaction conditions favor properly oriented collisions between reactant molecules. An increased probability of effectively oriented collisions results in larger values for *A* and faster reaction rates.

The exponential term, $e^{-Ea/RT}$, describes the effect of activation energy on reaction rate. According to kinetic molecular theory (see chapter on gases), the temperature of matter is a measure of the average kinetic energy of its constituent atoms or molecules. The distribution of energies among the molecules composing a sample of matter at any given temperature is described by the plot shown in Figure 2.3.5.3*a*. Two shaded areas under the curve represent the numbers of molecules possessing adequate energy (*RT*) to overcome the activation barriers (E_a). A lower activation energy results in a greater fraction of adequately energized molecules and a faster reaction.

The exponential term also describes the effect of temperature on reaction rate. A higher temperature represents a correspondingly greater fraction of molecules possessing sufficient energy (*RT*) to overcome the activation barrier (E_a), as shown in Figure 2.3.5.3*b*. This yields a greater value for the rate constant and a correspondingly faster reaction rate.

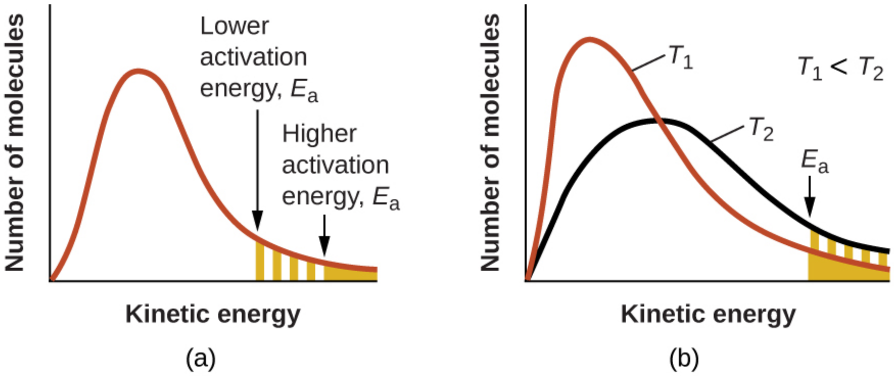


Figure 2.3.5.3: Molecular energy distributions showing numbers of molecules with energies exceeding (a) two different activation energies at a given temperature, and (b) a given activation energy at two different temperatures.

A convenient approach for determining E_a for a reaction involves the measurement of *k* at two or more different temperatures and using an alternate version of the Arrhenius equation that takes the form of a linear equation

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

$$y = mx + b$$

A plot of $\ln k$ versus $\frac{1}{T}$ is linear with a slope equal to $\frac{-E_a}{R}$ and a y-intercept equal to $\ln A$.

✓ Example 2.3.5.1: Determination of E_a

The variation of the rate constant with temperature for the decomposition of $\mathrm{HI(g)}$ to $\mathrm{H_2(g)}$ and $\mathrm{I_2(g)}$ is given here. What is the activation energy for the reaction?

$$2\,\mathrm{HI(g)} \longrightarrow \mathrm{H_2(g)} + \mathrm{I_2(g)}$$

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

Use the provided data to derive values of $\frac{1}{T}$ and $\ln k$:

$\frac{1}{T}$	$\ln k$
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 2.3.5.4is a graph of $\ln k$ versus $\frac{1}{T}$. In practice, the equation of the line (slope and *y*-intercept) that best fits these plotted data points would be derived using a statistical process called regression. This is helpful for most experimental data because a perfect fit of each data point with the line is rarely encountered. For the data here, the fit is nearly perfect and the slope may be estimated using any two of the provided data pairs. Using the first and last data points permits estimation of the slope.

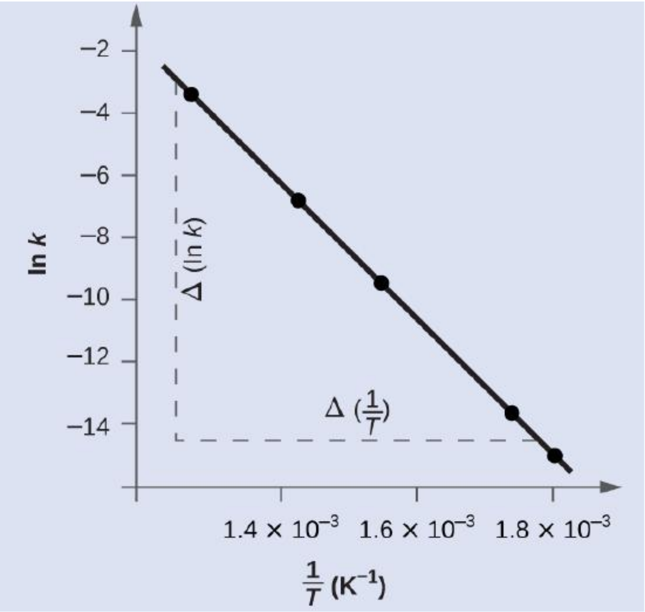


Figure 2.3.5.4: This graph shows the linear relationship between $\ln k$ versus $\frac{1}{T}$ for the reaction $2HI \longrightarrow H_2 + I_2$ according to the Arrhenius equation.

$$\begin{aligned}
\text{Slope} &= \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} \\
&= \frac{(-14.860)-(-3.231)}{\left(1.80\times10^{-3}K^{-1}\right)-\left(1.28\times10^{-3}K^{-1}\right)} \\
&= \frac{-11.629}{0.52\times10^{-3}K^{-1}} = -2.2\times10^{4}K \\
&= -\frac{E_a}{R} \\
E_a &= -\text{ slope }\times R = -\left(-2.2\times10^{4}K\times8.314Jmol^{-1}K^{-1}\right) \\
&\quad 1.8\times10^{5}Jmol^{-1}\text{ or }180kJmol^{-1}
\end{aligned}$$

Alternative approach: A more expedient approach involves deriving activation energy from measurements of the rate constant at just two temperatures. In this approach, the Arrhenius equation is rearranged to a convenient two-point form:

$$\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

Rearranging this equation to isolate activation energy yields:

$$E_a = -R\left(\frac{\ln k_2 - \ln k_1}{\left(\frac{1}{T_2}\right)-\left(\frac{1}{T_1}\right)}\right)$$

Any two data pairs may be substituted into this equation—for example, the first and last entries from the above data table:

$$E_a = -8.314Jmol^{-1}K^{-1}\left(\frac{-3.231-(-14.860)}{1.28\times10^{-3}K^{-1}-1.80\times10^{-3}K^{-1}}\right)$$

and the result is E_a = 1.8 10^5 J mol^{-1} or 180 kJ mol^{-1}

This approach yields the same result as the more rigorous graphical approach used above, as expected. In practice, the graphical approach typically provides more reliable results when working with actual experimental data.

? Exercise 2.3.5.1

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

1.1 10^5 J mol^{-1} or 110 kJ mol^{-1}

2.3.6: Reaction Mechanisms

Learning Objectives

By the end of this section, you will be able to:

- 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

Chemical reactions very often occur in a step-wise fashion, involving two or more distinct reactions taking place in sequence. A balanced equation indicates what is reacting and what is produced, but it reveals no details about how the reaction actually takes place. The reaction mechanism (or reaction path) provides details regarding the precise, step-by-step process by which a reaction occurs.

The decomposition of ozone, for example, appears to follow a mechanism with two steps:

$$O_3(g) \longrightarrow O_2(g) + O$$
$$O + O_3(g) \longrightarrow 2O_2(g)$$

Each of the steps in a reaction mechanism is an **elementary reaction**. These elementary reactions occur precisely as represented in the step equations, and they must sum to yield the balanced chemical equation representing the overall reaction:

$$2O_3(g) \longrightarrow 3O_2(g)$$

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 direct collision and reaction of two ozone molecules*. Instead, one O_3 decomposes to yield O_2 and an oxygen atom, and a second O_3 molecule subsequently reacts with the oxygen atom to yield two additional O_2 molecules.

Unlike balanced equations representing an overall reaction, the equations for elementary reactions are explicit representations of the chemical change taking place. The reactant(s) in an elementary reaction’s equation undergo only the bond-breaking and/or making events depicted to yield the product(s). For this reason, *the rate law for an elementary reaction may be derived directly from the balanced chemical equation describing the reaction*. This is not the case for typical chemical reactions, for which rate laws may be reliably determined only via experimentation.

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 reaction of a *single* reactant species to produce one or more molecules of product:

$$A \longrightarrow \text{ products}$$

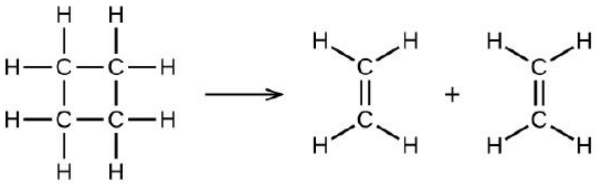
The rate law for a unimolecular reaction is first order:

$$\text{rate } = k[A]$$

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

$$O_3 \longrightarrow O_2 + O$$

illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism as described above. However, some unimolecular reactions may be the only step of a single-step reaction mechanism. (In other words, an “overall” reaction may also be an elementary reaction in some cases.) For example, the gas-phase decomposition of cyclobutane, C_4H_8, to ethylene, C_2H_4, is represented by the following chemical equation:



This equation represents the overall reaction observed, and it might also represent a legitimate unimolecular elementary reaction. The rate law predicted from this equation, assuming it is an elementary reaction, turns out to be the same as the rate law derived experimentally for the overall reaction, namely, one showing first-order behavior:

$$\text{rate } = -\frac{\Delta\left[C_4H_8\right]}{\Delta t} = k\left[C_4H_8\right]$$

This agreement between observed and predicted rate laws is interpreted to mean that the proposed unimolecular, single-step process is a reasonable mechanism for the butadiene reaction.

Bimolecular Elementary Reactions

A bimolecular reaction involves two reactant species, for example:

$$A + B \longrightarrow \text{ products}$$

and

$$2A \longrightarrow \text{ products}$$

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* (second-order overall):

$$\text{rate } = k[A][B]$$

For the second type, in which two identical molecules collide and react, the rate law is second order in *A*:

$$\text{rate } = k[A][A] = k[A]^2$$

Some chemical reactions occur by mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

(see Figure $2.3.6.1$)

Figure $2.3.6.1$: 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 the second step of the two-step ozone decomposition mechanism discussed earlier in this section:

$$O(g) + O_3(g) \longrightarrow 2O_2(g)$$

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:

$$2NO + O_2 \longrightarrow 2NO_2$$

$$\text{rate } = k[NO]^2\,[O_2]$$

Likewise, the reaction of nitric oxide with chlorine appears to involve termolecular steps:

$$2NO + Cl_2 \longrightarrow 2NOCl$$

$$\text{rate } = k[NO]^2\,[Cl_2]$$

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 $2.3.6.2$

Figure $2.3.6.2$: 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)

As described earlier, rate laws may be derived directly from the chemical equations for elementary reactions. This is not the case, however, for ordinary 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 mechanisms. In every case, the rate law must be determined from experimental data and the reaction mechanism subsequently deduced from the rate law (and sometimes from other data). The reaction of NO_2 and CO provides an illustrative example:

$$NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$$

For temperatures above 225 °C, the rate law has been found to be:

$$\text{rate } = k\,[NO_2]\,[CO]$$

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:

$$\text{rate } = k[NO_2]^2$$

This rate law is not consistent with the single-step mechanism, but is consistent with the following two-step mechanism:

$$NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g) \text{ (slow)}$$

$$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g) \text{ (fast)}$$

The rate-determining (slower) 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 a rapidly reversible reaction the rate law for the overall reaction may be more difficult to derive.

As discussed in several chapters of this text, a reversible reaction is at *equilibrium* when the rates of the forward and reverse processes are equal. Consider the reversible elementary reaction in which NO dimerizes to yield an intermediate species N_2O_2.

$$NO + NO \rightleftharpoons N_2O_2$$

When this reaction is at equilibrium:

$$\text{rate }_{\text{forward}} = \text{rate }_{\text{reverse}}$$
$$k_1[NO]^2 = k_{-1}\,[N_2O_2]$$

This expression may be rearranged to express the concentration of the intermediate in terms of the reactant NO:

$$\left(\frac{k_1[NO]^2}{k_{-1}}\right) = [N_2O_2]$$

Since intermediate species concentrations are not used in formulating rate laws for overall reactions, this approach is sometimes necessary, as illustrated in the following example exercise.

✓ Example 2.3.6.1: Deriving a Rate Law from a Reaction Mechanism

The two-step mechanism below has been proposed for a reaction between nitrogen monoxide and molecular chlorine:

$$\text{Step 1:}\quad \mathrm{NO(g) + Cl_2(g) \rightleftharpoons NOCl_2(g)} \qquad \text{(fast)}$$
$$\text{Step 2:}\quad \mathrm{NOCl_2(g) + NO(g) \rightleftharpoons 2\,NOCl(g)} \qquad \text{(slow)}$$

Use this mechanism to derive the equation and predicted rate law for the overall reaction.

Solution

The equation for the overall reaction is obtained by adding the two elementary reactions:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

To derive a rate law from this mechanism, first write rates laws for each of the two steps.

$$\text{rate }_1 = k_1[NO]\,[Cl_2] \text{ for the forward reaction of step 1}$$
$$\text{rate }_{-1} = k_{-1}\,[NOCl_2] \text{ for the reverse reaction of step 1}$$
$$\text{rate }_2 = k_2\,[NOCl_2]\,[NO] \text{ for step 2}$$

Step 2 is the rate-determining step, and so the rate law for the overall reaction should be the same as for this step. However, the step 2 rate law, as written, contains an intermediate species concentration, $[NOCl_2]$. To remedy this, use the first step's rate laws to derive an expression for the intermediate concentration in terms of the reactant concentrations.

Assuming step 1 is at equilibrium:

$$\text{rate }_1 = \text{rate }_{-1}$$
$$k_1[NO]\,[Cl_2] = k_{-1}\,[NOCl_2]$$
$$[NOCl_2] = \left(\frac{k_1}{k_{-1}}\right)[NO]\,[Cl_2]$$

Substituting this expression into the rate law for step 2 yields:

$$\text{rate }_2 = \text{rate }_{\text{overall}} = \left(\frac{k_2k_1}{k_{-1}}\right)[NO]^2\,[Cl_2]$$

Exercise 2.3.6.1

The first step of a proposed multistep mechanism is:

\ce{F2(g) <=> 2 F(g) \tag{fast}}

Derive the equation relating atomic fluorine concentration to molecular fluorine concentration.

Answer

$$[\mathrm{F}]=\left(\frac{k_1\left[F_2\right]}{k_{-1}}\right)^{1/2}$$

2.3.7: Catalysis

Learning Objectives

By the end of this section, you will be able to:

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

Among the factors affecting chemical reaction rates discussed earlier in this chapter was the presence of a *catalyst*, a substance that can increase the reaction rate without being consumed in the reaction. The concepts introduced in the previous section on reaction mechanisms provide the basis for understanding how catalysts are able to accomplish this very important function.

Figure $2.3.7.1$ shows reaction diagrams for a chemical process in the absence and presence of a catalyst. Inspection of the diagrams reveals several traits of these reactions. Consistent with the fact that the two diagrams represent the same overall reaction, both curves begin and end at the same energies (in this case, because products are more energetic than reactants, the reaction is endothermic). The reaction mechanisms, however, are clearly different. The uncatalyzed reaction proceeds via a one-step mechanism (one transition state observed), whereas the catalyzed reaction follows a two-step mechanism (two transition states observed) with *a notably lesser activation energy*. This difference illustrates the means by which a catalyst functions to accelerate reactions, namely, by providing an alternative reaction mechanism with a lower activation energy. Although the catalyzed reaction mechanism for a reaction needn't necessarily involve a different number of steps than the uncatalyzed mechanism, it must provide a reaction path whose rate determining step is faster (lower E_a).

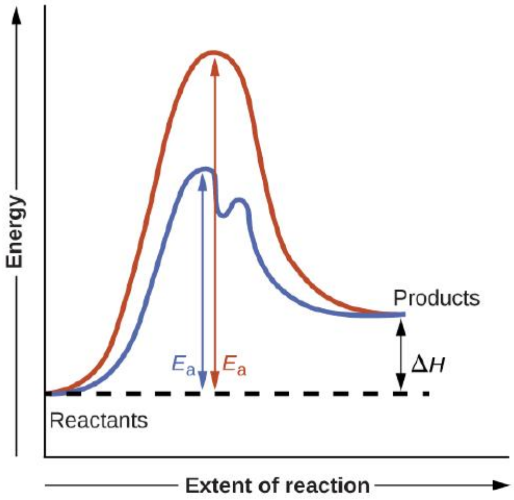
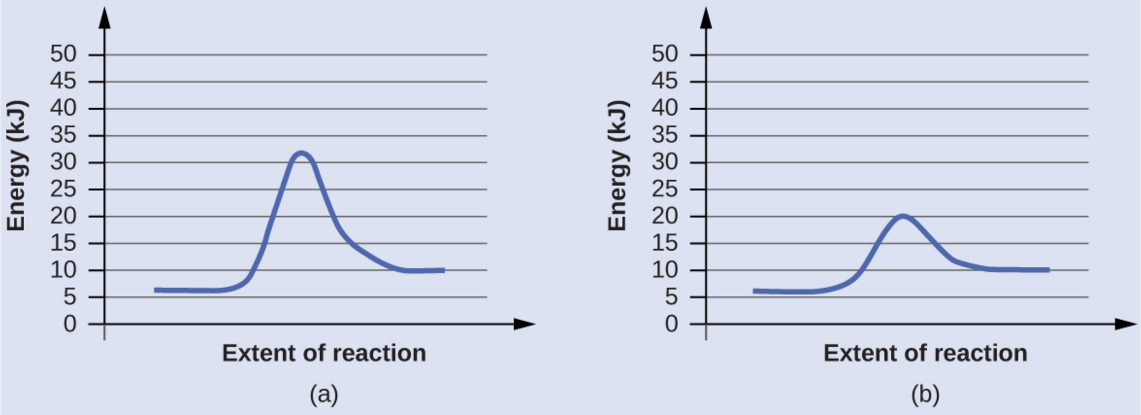


Figure $2.3.7.1$: Reaction diagrams for an endothermic process in the absence (red curve) and presence (blue curve) of a catalyst. The catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

Example $2.3.7.1$: Reaction Diagrams for Catalyzed Reactions

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Estimate the activation energy for each process, and identify which one involves a catalyst.



Solution

Activation energies are calculated by subtracting the reactant energy from the transition state energy.

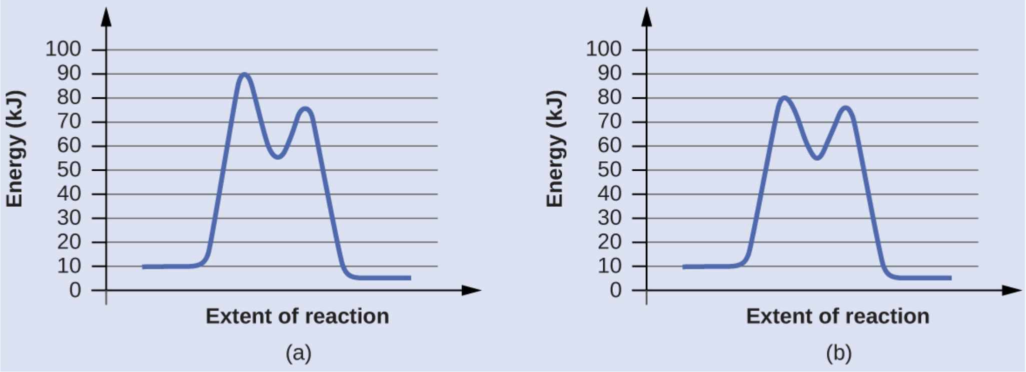
$$\text{diagram}(a): E_a = 32kJ - 6kJ = 26kJ$$

$$\text{diagram}(b): E_a = 20kJ - 6kJ = 14kJ$$

The catalyzed reaction is the one with lesser activation energy, in this case represented by diagram b.

? Exercise 2.3.7.1

Reaction diagrams for a chemical process with and without a catalyst are shown below. Both reactions involve a two-step mechanism with a rate-determining first step. Compute activation energies for the first step of each mechanism, and identify which corresponds to the catalyzed reaction. How do the second steps of these two mechanisms compare?



Answer

For the first step, E_a = 80 kJ for (a) and 70 kJ for (b), so diagram (b) depicts the catalyzed reaction. Activation energies for the second steps of both mechanisms are the same, 20 kJ.

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:

$$3O_2(g) \xrightarrow{hv} 2O_3(g)$$

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 two-step mechanism:

$$O_3 \longrightarrow O_2 + O$$
$$O + O_3 \longrightarrow 2O_2$$

A number of substances can catalyze the decomposition of ozone. For example, the nitric oxide–catalyzed decomposition of ozone is believed to occur via the following three-step mechanism:

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$
$$O_3(g) \longrightarrow O_2(g) + O(g)$$
$$NO_2(g) + O(g) \longrightarrow NO(g) + O_2(g)$$

As required, the overall reaction is the same for both the two-step uncatalyzed mechanism and the three-step NO-catalyzed mechanism:

$$2O_3(g) \longrightarrow 3O_2(g)$$

Notice that NO is a reactant in the first step of the mechanism and a product in the last step. This is another characteristic trait of a catalyst: Though it participates in the chemical reaction, it is not consumed by the reaction.

Portrait of a Chemist: Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina (Figure $2.3.7.2$), and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone."[1] Molina's initial discovery of stratospheric depletion of ozone by chlorine atoms was done at the University of California Irvine, he later moved to the NASA/Jet Propulsion Laboratory, MIT and the University of California, San Diego. At the time of his death in 2020 Molina, a Mexican citizen had established a new center for the study of energy and the environment in Mexico City.

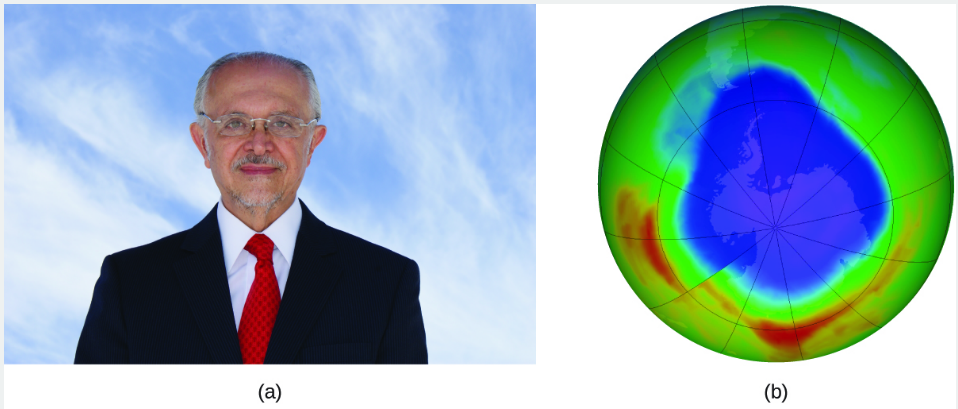


Figure $2.3.7.2$: (a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his (b) early research on stratospheric depletion of ozone and later the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

In 1974, Molina and Rowland published a paper in the journal *Nature* 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:

$$CH_3Cl + OH \longrightarrow Cl + \text{ other products} \tag{2.3.7.1}$$

Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:

$$Cl + O_3 \longrightarrow ClO + O_2$$

$$ClO + O \longrightarrow Cl + O_2$$

overall Reaction: $O_3 + O \longrightarrow 2O_2$ \nonumber \]

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 $ClONO_2$.

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 12.21, is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells (Figure $2.3.7.4$).

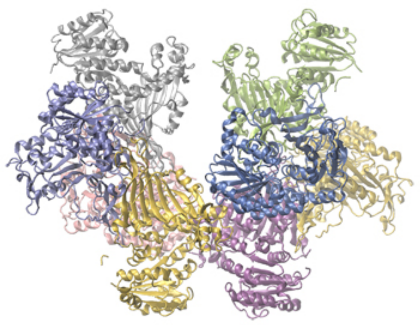


Figure 12.21 Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

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.

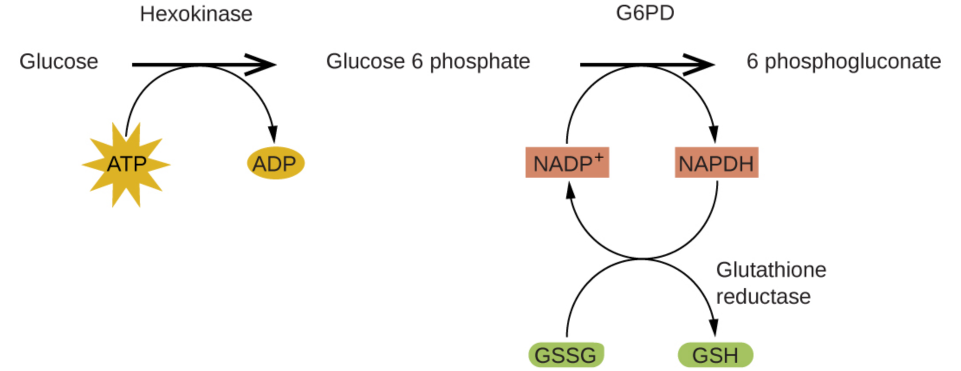


Figure $2.3.7.4$: In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NADPH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

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 typically involves the following processes:

1. Adsorption of the reactant(s) onto the surface of the catalyst
2. Activation of the adsorbed reactant(s)
3. Reaction of the adsorbed reactant(s)

Figure 2.3.7.5 illustrates the steps of a mechanism for 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).

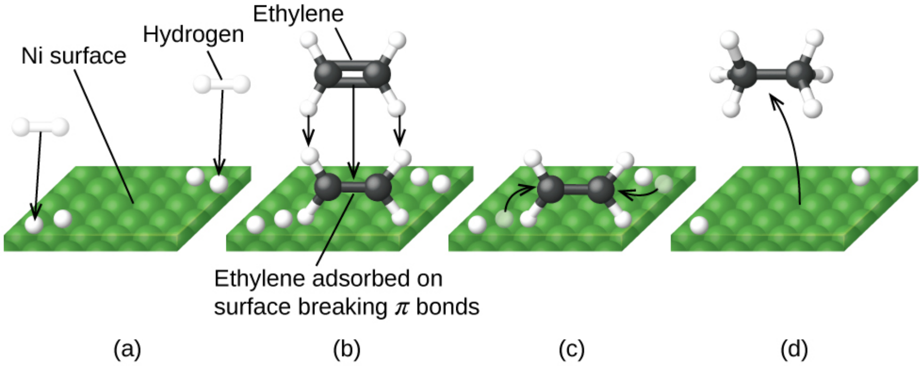


Figure 2.3.7.5: Mechanism for the Ni-catalyzed reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the C–C π-bond and forming Ni–C bonds. (c) Atoms diffuse across the surface and form new C–H bonds when they collide. (d) C_2H_6 molecules desorb from the Ni surface.

Many important chemical products are prepared via industrial processes that use heterogeneous catalysts, including ammonia, nitric acid, sulfuric acid, and methanol. Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles (Figure 2.3.7.6).

Chemistry in Everyday Life: Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. 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 2.3.7.6).

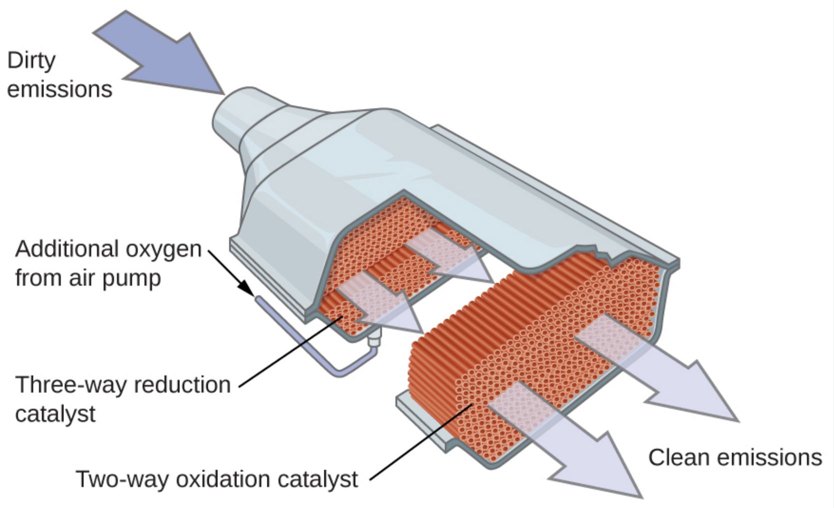


Figure 2.3.7.6: A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion of 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:

$$2NO_2(g) \longrightarrow N_2(g) + 2O_2(g)$$

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$

$$2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

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.

Link to Learning

The LibreTexts provides a thorough explanation of how catalytic converters work.

How Sciences Interconnect: 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 $2.3.7.1$

Table $2.3.7.1$: 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 $2.3.7.7$).

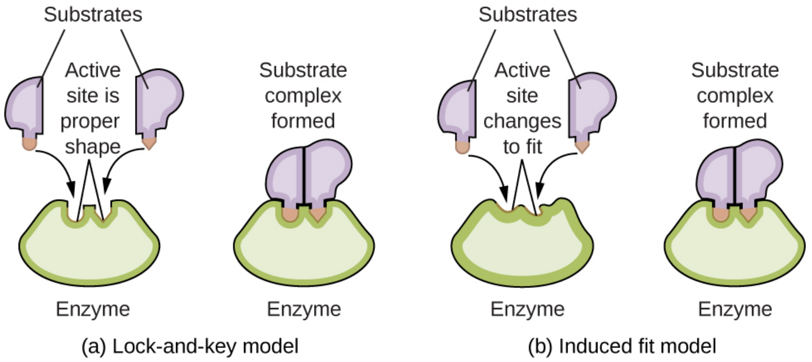


Figure $2.3.7.7$: (a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

Link to Learning

The Royal Society of Chemistry provides an excellent introduction to enzymes for students and teachers.

Footnotes

- 1“The Nobel Prize in Chemistry 1995,” Nobel Prize.org, accessed February 18, 2015, http://www.nobelprize.org/nobel_priz...aureates/1995/.

CHAPTER OVERVIEW

3: The First Law of Thermodynamics

3.1: Overview of Classical Thermodynamics

One of the pioneers in the field of modern thermodynamics was James P. Joule (1818 - 1889). Among the experiments Joule carried out, was an attempt to measure the effect on the temperature of a sample of water that was caused by doing work on the water. Using a clever apparatus to perform work on water by using a falling weight to turn paddles within an insulated canister filled with water, Joule was able to measure a temperature increase in the water.

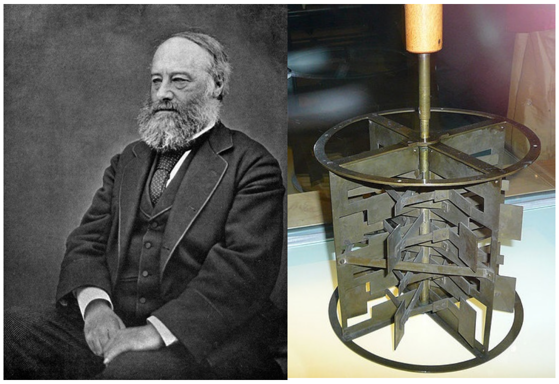


Figure $3.1.1$: (left) James Prescott Joule (1818 - 1889) (right) Joule's apparatus for measuring the work equivalent of heat. (CC BY-SA 3.0; Dr. Mirko Junge)

Thus, Joule was able to show that work and heat can have the same effect on matter – a change in temperature! It would then be reasonable to conclude that heating, as well as doing work on a system will increase its energy content, and thus it's ability to perform work in the surroundings. This leads to an important construct of the **First Law of Thermodynamics**:

> *The capacity of a system to do work is increased by heating the system or doing work on it.*

The **internal energy** (U) of a system is a measure of its capacity to supply energy that can do work within the surroundings, making U the ideal variable to keep track of the flow of heat and work energy into and out of a system. Changes in the internal energy of a system (ΔU) can be calculated by

$$\Delta U = U_f - U_i \tag{3.1.1}$$

where the subscripts i and f indicate initial and final states of the system. U as it turns out, is a state variable. In other words, the amount of energy available in a system to be supplied to the surroundings is independent on how that energy came to be available. That's important because the manner in which energy is transferred is path dependent.

There are two main methods energy can be transferred to or from a system. These are suggested in the previous statement of the first law of thermodynamics. Mathematically, we can restate the first law as

$$\Delta U = q + w$$

or

$$dU = dq + dw$$

where q is defined as the amount of energy that flows into a system in the form of **heat** and w is the amount of energy lost due to the system doing **work** on the surroundings.

3.1.1: Heat

Heat is the kind of energy that in the absence of other changes would have the effect of changing the temperature of the system. A process in which heat flows into a system is **endothermic** from the standpoint of the system ($q_{system} > 0$, $q_{surroundings} < 0$). Likewise, a process in which heat flows out of the system (into the surroundings) is called **exothermic** ($q_{system} < 0$, $q_{surroundings} > 0$). In the absence of any energy flow in the form or work, the flow of heat into or out of a system can be measured by a change in temperature. In cases where it is difficult to measure temperature changes of the system directly, the amount of heat energy transferred in a process can be measured using a change in temperature of the soundings. (This concept will be used later in the discussion of calorimetry).

An infinitesimal amount of heat flow into or out of a system can be related to a change in temperature by

$$dq = C\,dT$$

where C is the **heat capacity** and has the definition

$$C = \frac{dq}{\partial T}$$

Heat capacities generally have units of (J mol^{-1} K^{-1}) and magnitudes equal to the number of J needed to raise the temperature of 1 mol of substance by 1 K. Similar to a heat capacity is a **specific heat** which is defined per unit mass rather than per mol. The specific heat of water, for example, has a value of 4.184 J g^{-1} K^{-1} (at constant pressure – a pathway distinction that will be discussed later.)

✓ Example 3.1.1: Heat required to Raise Temperature

How much energy is needed to raise the temperature of 5.0 g of water from 21.0 °C to 25.0 °C?

Solution

$$\begin{aligned} q &= mC\Delta T \\ &= (5.0\ \cancel{g})(4.184 \frac{J}{\cancel{g}\ {}^{\circ}\cancel{C}})(25.0\ {}^{\circ}\cancel{C} - 21.0\ {}^{\circ}\cancel{C}) \\ &= 84\ J \end{aligned}$$

What is a partial derivative?

A partial derivative, like a total derivative, is a slope. It gives a magnitude as to how quickly a function changes value when one of the dependent variables changes. Mathematically, a partial derivative is defined for a function $f(x_1, x_2, \ldots x_n)$ by

$$\left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq i} = \lim_{\Delta_i \to 0} \left(\frac{f(x_1 + \Delta x_1, x_2 + \Delta x_2, \ldots, x_i + \Delta x_i, \ldots x_n + \Delta x_n) - f(x_1, x_2, \ldots x_i, \ldots x_n)}{\Delta x_i} \right)$$

Because it measures how much a function changes for a change in a given dependent variable, infinitesimal changes in the in the function can be described by

$$df = \sum_i \left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq i}$$

So that each contribution to the total change in the function f can be considered separately.

For simplicity, consider an ideal gas. The pressure can be calculated for the gas using the ideal gas law. In this expression, pressure is a function of temperature and molar volume.

$$p(V,T) = \frac{RT}{V}$$

The partial derivatives of p can be expressed in terms of T and V as well.

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{V^2} \tag{3.1.2}$$

and

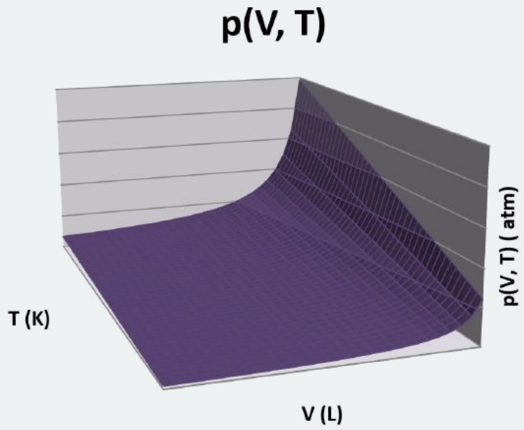
$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} \tag{3.1.3}$$

So that the change in pressure can be expressed

$$dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT \tag{3.1.4}$$

or by substituting Equations 3.1.2 and 3.1.3

$$dp = \left(-\frac{RT}{V^2}\right) dV + \left(\frac{R}{V}\right) dT$$



Macroscopic changes can be expressed by integrating the individual pieces of Equation 3.1.4 over appropriate intervals.

$$\Delta p = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial V}\right)_T dV + \int_{T_1}^{T_2} \left(\frac{\partial p}{\partial T}\right)_V dT$$

This can be thought of as two consecutive changes. The first is an **isothermal** (constant temperature) expansion from V_1 to V_2 at T_1 and the second is an **isochoric** (constant volume) temperature change from T_1 to T_2 at V_2. For example, suppose one needs to calculate the change in pressure for an ideal gas expanding from 1.0 L/mol at 200 K to 3.0 L/mol at 400 K. The set up might look as follows.

$$\Delta p = \underbrace{\int_{V_1}^{V_2} \left(-\frac{RT}{V^2}\right) dV}_{\text{isothermal expansion}} + \underbrace{\int_{T_1}^{T_2} \left(\frac{R}{V}\right) dT}_{\text{isochoric heating}}$$

or

$$\begin{aligned}\Delta p &= \int_{1.0\ L/mol}^{3.0\ L/mol} \left(-\frac{R(400\ K)}{V^2}\right) dV + \int_{200\ K}^{400,\ K} \left(\frac{R}{1.0\ L/mol}\right) dT \\ &= \left[\frac{R(200\ K)}{V}\right]_{1.0\ L/mol}^{3.0\ L/mol} + \left[\frac{RT}{3.0\ L/mol}\right]_{200\ K}^{400\ K} \\ &= R\left[\left(\frac{200\ K}{3.0\ L/mol} - \frac{200\ K}{1.0\ L/mol}\right) + \left(\frac{400\ K}{3.0\ L/mol} - \frac{200\ K}{3.0\ L/mol}\right)\right] \\ &= -5.47\ atm\end{aligned}$$

Alternatively, one could calculate the change as an isochoric temperature change from T_1 to T_2 at V_1 followed by an isothermal expansion from V_1 to V_2 at T_2:

$$\Delta p = \int_{T_1}^{T_2} \left(\frac{R}{V}\right) dT + \int_{V_1}^{V_2} \left(-\frac{RT}{V^2}\right) dV$$

or

$$\begin{aligned}\Delta p &= \int_{200\,K}^{400,\,K} \left(\frac{R}{1.0\,L/mol}\right) dT + \int_{1.0\,L/mol}^{3.0\,L/mol} \left(-\frac{R(400\,K)}{V^2}\right) dV \\ &= \left[\frac{RT}{1.0\,L/mol}\right]_{200\,K}^{400\,K} + \left[\frac{R(400\,K)}{V}\right]_{1.0\,L/mol}^{3.0\,L/mol} \\ &= R\left[\left(\frac{400\,K}{1.0\,L/mol} - \frac{200\,K}{1.0\,L/mol}\right) + \left(\frac{400\,K}{3.0\,L/mol} - \frac{400\,K}{1.0\,L/mol}\right)\right] \\ &= -5.47\,atm\end{aligned}$$

This results demonstrates an important property of pressure in that pressure is a state variable, and so the calculation of changes in pressure do not depend on the pathway!

3.1.2: Work

Work can take several forms, such as expansion against a resisting pressure, extending length against a resisting tension (like stretching a rubber band), stretching a surface against a surface tension (like stretching a balloon as it inflates) or pushing electrons through a circuit against a resistance. The key to defining the work that flows in a process is to start with an infinitesimal amount of work defined by what is changing in the system.

Table 3.1.1: Changes to the System

Type of work	Displacement	Resistance	dw
Expansion	dV (volume)	-p_{ext} (pressure)	-p_{ext}dV
Electrical	dQ (charge)	W (resistence)	-W dQ
Extension	dL (length)	-t (tension)	t dL
Stretching	dA	-s (surf. tens.)	sdA

The pattern followed is always an infinitesimal displacement multiplied by a resisting force. The total work can then be determined by integrating along the pathway the change follows.

Example 3.1.2: Work from a Gas Expansion

What is the work done by 1.00 mol an ideal gas expanding from a volume of 22.4 L to a volume of 44.8 L against a constant external pressure of 0.500 atm?

Solution

$$dw = -p_{ext}\,dV$$

since the pressure is constant, we can integrate easily to get total work

$$\begin{aligned}w &= -p_{exp}\int_{V_1}^{V_2} dV \\ &= -p_{exp}(V_2 - V_1) \\ &= -(0.500\,am)(44.8\,L - 22.4\,L)\left(\frac{8.314\,J}{0.08206\,atm\,L}\right) \\ &= -1130\,J = -1.14\,kJ\end{aligned}$$

Note: The ratio of gas law constants can be used to convert between atm·L and J quite conveniently!

3.2: Pressure-Volume Work

Work in general is defined as a product of a force $\mathbf{F}$ and a path element $\mathbf{ds}$. Both are vectors and work is computed by integrating over their inner product:

$$w = \int \mathbf{F} \cdot \mathbf{ds}$$

Moving an object against the force of friction as done in the above dissipation experiment is but one example of work:

$$w_{friction} = \int \mathbf{F}_{\text{friction}} \cdot \mathbf{ds}$$

We could also think of *electrical* work. In that case we would be moving a charge *e* (e.g. the negative charge of an electron) against an electrical (vector) field $\mathbf{E}$. The work would be:

$$w_{electical} = \int e\mathbf{E} \cdot \mathbf{ds}$$

Other examples are the stretching of a rubber band against the elastic force or moving a magnet in a magnetic field etc, etc.

Pressure-volume (PV) work

In the case of a cylinder with a piston, the pressure of gas molecules on the inside of the cylinder, P, and the gas molecules external to the piston, P_{ext} both exert a force against each other. Pressure, (\P\), is the force, F, being exerted by the particles per area, A:

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

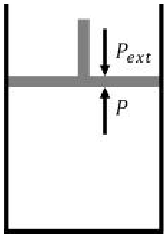


Figure 19.2.1 : A piston with internal pressure P and external pressure P_{ext}.

We can assume that all the forces generated by the pressure of the particles operate parallel to the direction of motion of the piston. That is, the force moves the piston up or down as the movement of the piston is constrained to one direction. The piston moves as the molecules of the gas rapidly equilibrate to the applied pressure such that the internal and external pressures are the same. The result of this motion is work:

$$w_{volume} = \int \left(\frac{F}{A}\right)(A\,ds) = \int P\,dV \tag{3.2.1}$$

This particular form of work is called **pressure-volume (PV) work** and will play an important role in the development of our theory. Notice however that volume work is only ***one form*** of work.

Sign Conventions

It is important to create a sign convention at this point: positive heat, positive work is always energy you put in into the system. If the system decides to remove energy by giving off heat or work, that gets a minus sign.

In other words: ***you pay the bill***.

To comply with this convention we need to rewrite volume work (Equation 3.2.1) as

$$w_{PV} = -\int \left(\frac{F}{A}\right)(A\,ds) = -\int P\,dV$$

> Hence, to decrease the volume of the gas (ΔV is negative), we must put in (positive) work.

Thermodynamics would not have come very far without cylinders to hold gases, in particular steam. The following figure shows when the external pressure, P_{ext}, is greater than and less than the internal pressure, P, of the piston.

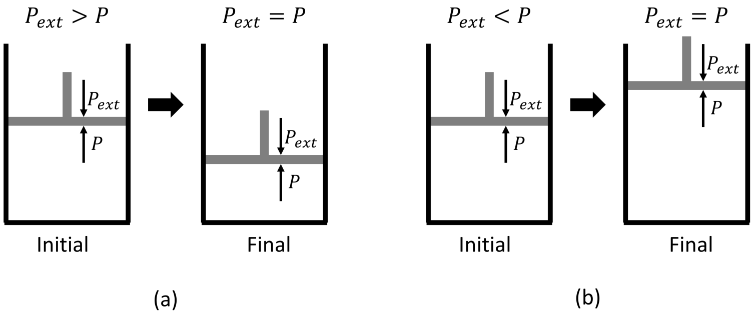


Figure 19.2.2 : Pistons showing a compression (left) and an expansion (right).

If the pressure, P_{ext}, being exerted on the system is constant, then the integral becomes:

$$w = -P_{\text{ext}} \int_{V_{initial}}^{V_{final}} dV = -P_{\text{ext}} \Delta V \tag{3.2.2}$$

Since the system pressure (inside the piston) is not the same as the pressure exerted on the system, the system is not in a state of equilibrium and cannot be shown directly on and PV diagram. This type of process is called an irreversible process. For a system that undergoes irreversible work at constant external pressure, we can show the amount of work being done on a PV diagram despite not being able to show the process itself.

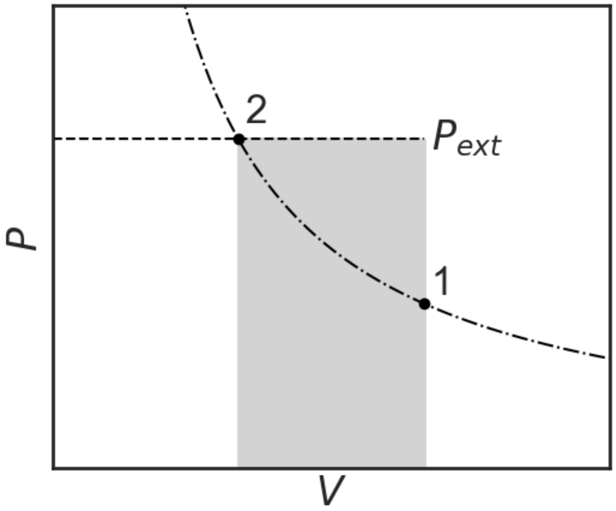


Figure 19.2.3 : A system is compressed under constant external pressure, P_{ext}, from state 1 to state 2. The shaded area shows the amount of work being done for the compression. The dash-dot line is an isotherm, a path of constant temperature, showing that the initial and final temperature of the irreversible compression are the same.

Note that the external pressure, P_{ext}, exerted on the system is constant. If the external pressure changes during the compression, we must *integrate* over the whole range:

$$w = -\int_{V_{initial}}^{V_{final}} P_{\text{ext}}(V)\, dV$$

3.3: Work and Heat are not State Functions

3.3.1: Heat and work are path functions

Heat (q) and work (w) are path functions, not state functions:

1. They are path dependent.
2. They are energy transfer → they are not intrinsic to the system.

Path Functons

Functions that depend on the path taken, such as work (w) and heat (q), are referred to as **path functions**.

3.3.2: Reversible versus irreversible

Let's consider a piston that is being compressed at constant temperature (isothermal) to half of its initial volume:

1. Start with cylinder 1 liter, both external and internal pressure 1 bar.
2. ***Peg*** the piston in a fixed position.
3. Put cylinder in a pressure chamber with $P_{ext} = 2$ bar.
4. Suddenly pull the peg.

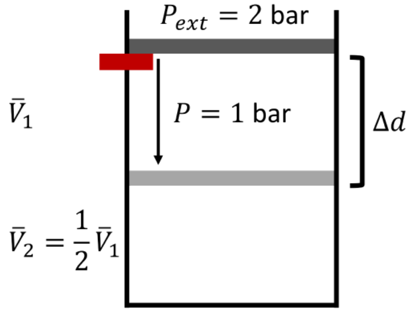


Figure 19.3.1 : A piston is being irreversibly and isothermally compressed under constant external pressure from state 1 to state 2.

The piston will shoot down till the internal and external pressures balance out again and the volume is 1/2 L. Notice that the external pressure was ***maintained*** constant at 2 bar during the peg-pulling and that the internal and external pressures were ***not*** balanced at all time. In a $P-V$ diagram of an ideal gas, P is a hyperbolic function of V under constant temperature (isothermal), but this refers to the *internal* pressure of the gas. It is the external one that counts when computing work and they are not necessarily the same. As long as $P_{external}$ is constant, work is represented by a rectangle.

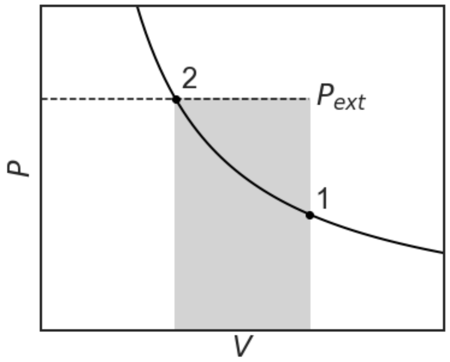


Figure 19.3.1 : The system is being irreversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area.

The amount of work being done is equal to the shaded region and in equation:

$$w = -\int_{V_1}^{V_2} PdV = -P_{ext}\left(V_2 - V_1\right) = -P\Delta V$$

This represents the maximum amount of work that can be done for an isothermal compression. Work is being done on the system, so the overall work being done is positive. Let's repeat the experiment, but this time the piston will compress reversibly over infinitesimally small steps where the $P_{ext} = P_{system}$:

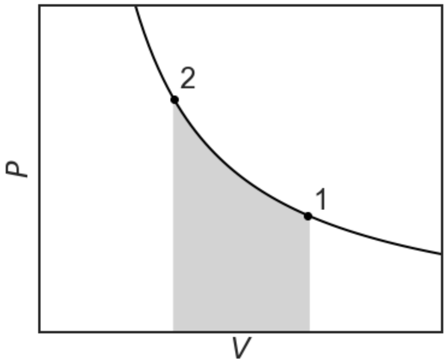


Figure 19.3.1 : The system is being reversibly and isothermally compressed from state 1 to 2. The amount of work being done on the system is shown by the shaded area. Note that for a compression, a reversible process does less work than an irreversible process.

For an ideal gas, the amount of work being done along the reversible compression is:

$$w = -\int_{V_1}^{V_2} PdV = -nRT\int_{V_1}^{V_2} \frac{1}{V} = -nRT\ln\left(\frac{V_2}{V_1}\right)$$

The amount of work being done to the two systems are not the same in the two diagrams (see the gray areas). Work is not a state, but a path function, as it depends on the path taken. You may say, what's the big difference. In both cases, the system is compressed from state 1 to state 2. The key is the word ***suddenly***. By pegging the position in place for the first compression, we have created a situation where the external pressure is higher than the internal pressure ($P_{ext} > P$). Because work is done suddenly by pulling the peg out, the internal pressure is struggling to catch up with the external one. During the second compression, we have $P_{ext} = P$ at all times. It's a bit like falling off a cliff versus gently sliding down a hill. Path one is called an irreversible path, the second a reversible path.

Reversible vs. Irreversible Processes

A reversible path is a path that follows a series of states at rest (i.e., the forces are allowed to balance at all times). In an irreversible one the forces only balance at the very end of the process.

Notice that less work is being done on the reversible isothermal compression than the one-step irreversible isothermal compression. In fact, the minimum amount of work that can be done during a compression always occurs along the reversible path.

3.3.2.1: Isothermal Expansion

Let's consider a piston that is being expanded at constant temperature (isothermal) to twice of its initial volume:

1. Start with cylinder 1 liter in a pressure chamber with both an external and internal pressure of 2 bar.
2. ***Peg*** the piston in a fixed position.
3. Take the cylinder out of the pressure chamber with P_{ext}= 1 bar.
4. Suddenly pull the peg.

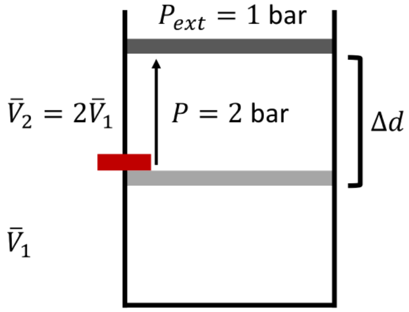


Figure 19.3.1 : A piston is being irreversibly and isothermally expanded under constant external pressure from state 1 to state 2.

The piston will shoot up till the internal and external pressures balance out again and the volume is 2 L. Notice that the external pressure was ***maintained*** constant at 1 bar during the peg-pulling and that the internal and external pressures were ***not*** balanced at all time.

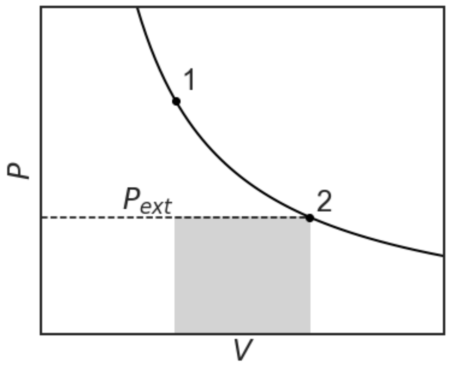


Figure 19.3.1 : The system is being irreversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area.

The amount of irreversible work being done is again equal to the shaded region and the equation:

$$w = -P\Delta V = -P_{ext}(V_2 - V_1) = -P\Delta V$$

This represents the minimum amount of work that can be done for an isothermal expansion. Work is being done on the system, so the overall work being done is negative. Let's repeat the experiment, but this time the piston will compress reversibly over infinitesimally small steps where the $P_{ext} = P_{system}$:

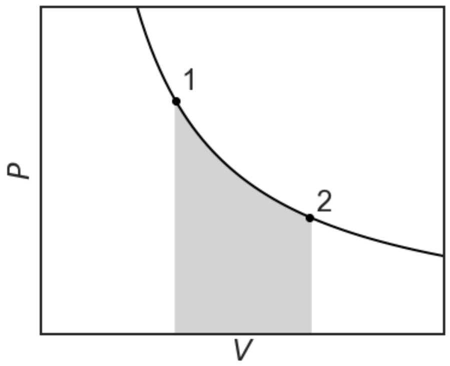


Figure 19.3.1 : The system is being reversibly and isothermally expanded from state 1 to 2. The amount of work being done by the system is shown by the shaded area. Note that for an expansion, a reversible process does more work than an irreversible process.

Notice that not only is more work is being done than the one-step irreversible isothermal expansion, but it is the same amount of work being done as the reversible isothermal compression. This is the maximum amount of work that can be done during an expansion.

3.4: Energy is a State Function

3.4.1: Work and heat are not state functions

> **A Better Definition of the First law of thermodynamics**
>
> The change in internal energy of a system is the sum of w and q, which is a state function.

The realization that work and heat are both forms of energy transfer undergoes quite an extension by saying that internal energy is a state function. It means that although heat and work can be produced and destroyed (and transformed into each other), energy is conserved. This allows us to do some serious bookkeeping! We can write the law as:

$$\Delta U = w + q$$

But the (important!) bit about the state function is better represented if we talk about small changes of the energy:

$$dU = \delta w + \delta q$$

We write a straight Latin d for U to indicate when the change in a state function, where as the changes in work and heat are path-dependent. This is indicated by the 'crooked' δ. We can represent changes as integrals, but only for U can we say that regardless of path we get $\Delta U = U_2 - U_1$ if we go from state one to state two. (I.e. it only depends on the end points, not the path).

> Notice that when we write dU or δq, we always mean infinitesimally small changes, i.e. we are implicitly taking a limit for the change approaching zero. To arrive at a macroscopic difference like ΔU or a macroscopic (finite) amount of heat q or work w **we need to integrate**.

We will now invoke the **first law of thermodynamics**:

- $dU = \delta q + \delta w$
- $\oint dU = 0$
- Internal energy is conserved

These are all ways of saying that internal energy is a state function.

3.5: An Adiabatic Process is a Process in which No Energy as Heat is Transferred

3.5.1: Isothermal expansion of an ideal gas

For a monatomic ideal gas we have seen that energy $\langle E\rangle$ observed as $U = 3/2nRT$. This means that energy is only dependent on temperature and if a gas is compressed **isothermally**, then the internal energy does not change:

$$\Delta U_{isothermal-idealgas} = 0$$

This means that the reversible work must ***cancel*** the reversible heat:

$$\Delta U_{rev} = w_{rev} + q_{rev} = 0$$

Therefore

$$w_{rev} = -q_{rev}$$

so from the expression of the reversible work for expansion in the last section

$$q_{rev} = nRT\ln\frac{V_2}{V_1}$$

If $V_2 > V_1$ (expansion), then you (or the environment) **must** put heat into the system because this is a positive number.

3.5.2: Adiabatic expansion of an ideal gas

Now suppose you make sure that no heat can enter the cylinder. (Put it in styrofoam or so). Then the path can still be reversible (slow pulling) but the process is then adiabatic.

> *This bat- part comes from a Greek verb βαινω (baino) that means walking, compare acro**bat**, someone who goes high places (acro-). The δια (dia) part means 'through' (cf. diagram, diorama, diagonal etc.) and the prefix α- (a-) denies it all (compare atypical versus typical).*

So the styrofoam prevents the heat from walking through the wall. When expanding the gas from V_1 to V_2 it still does reversible work but where does that come from? It can only come from the internal energy itself. So in this case any energy change should consist of work (adiabatic means: $\delta q = 0$).

$$dU = \delta w_{rev}$$

This implies that the temperature must drop, because if U changes, then T must change.

The change of energy with temperature at constant volume is known as the heat capacity (at constant volume) C_v

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

For an ideal gas U only changes with temperature, so that

Image:CH431_Image61.gif

or:

Image:CH431_Image62.gif

We can now compare two paths to go from state P_1, V_1, T_1 to state P_2, V_2, T_1:

1. Reversible isothermal expansion A
2. Reversible adiabatic expansion B followed by reversible isochoric heating C

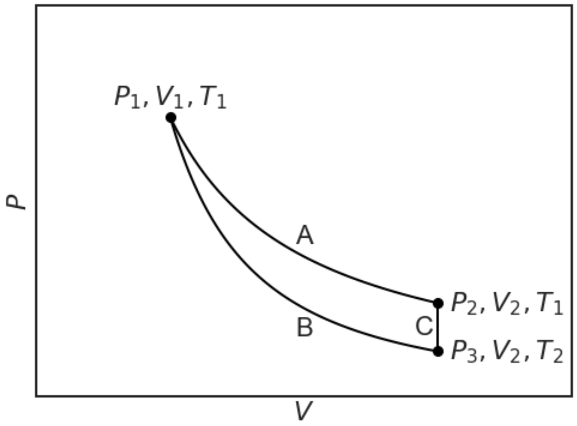


Figure __:

Notice that the temperature remains T_1 for path A (isotherm!), but that it drops to T_2 on the adiabat B, so that the cylinder has to be isochorically warmed up, C, to regain the same temperature.

ΔU_{tot} should be the same for both path A and the combined path B+C, because the end points are the same (U is a state function!). As the and points are at the same temperature and U only depends on T:

$$\Delta U_{tot} = 0$$

Along adiabat B:

$$q_{rev} = 0$$

Along isochoric heating C, there is no volume work because the volume is kept constant, so that:

Image:CH431_Image63.gif

This is the only reversible heat involved in path B+C. However, we know that ΔU_{tot} for path A is zero (isothermal!). This means that the volume work along B must cancel the heat along C:

The book keeping looks as follows, all paths are reversible:

$$\Delta U_{B+C} = \Delta U_A = 0 = q_B + w_B + q_C + w_C$$

We know that $q_B = 0$ since it is an adiabat and $w_C = 0$ since it is an isochore:

$$\Delta U_{B+C} = \Delta U_A = 0 = 0 + w_B + q_C + 0$$

Therefore:

$$w_B = -q_C$$

We had already seen before that along the isotherm A:

$$w_A = -q_A = -nRT \ln \frac{V_1}{V_2}$$

As you can see \w_A\) and w_B are ***not*** the same. Work is a path function, even if reversible. As we are working with an ideal gas we can be more precise about w_B and q_c as well. The term w_B along the adiabat is reversible volume work. Since there is no heat along B we can write a straight d instead of δ for the work contributions (It is the only contribution and must be identical to the state function dU):

Image:CH431_Image64.gif

3.6: The Temperature of a Gas Decreases in a Reversible Adiabatic Expansion

We can make the same argument for the heat along C. If we do the three processes A and B+C only to a tiny extent we can write:

Image:CH431_Image65.gif

And now we can integrate from V_1 to V_2 over the reversible adiabatic work along B and from T_1 to T_2 for the reversible isochoric heat along C. To separate the variables we do need to bring the temperature to the right side of the equation.:

Image:CH431_Image66.gif

The latter expression is valid for a reversible adiabatic expansion of a monatomic ideal gas (say Argon) because we used the C_v expression for such a system. We can use the gas law $PV = nRT$ to translate this expression in one that relates pressure and volume see Eq 19.23

We can mathematically show that the temperature of a gas decreases during an adiabatic expansion. Assuming an ideal gas, the internal energy along an adiabatic path is:

$$\begin{aligned} d\bar{U} &= \delta q + \delta w \\ &= 0 - Pd\bar{V} \\ &= -Pd\bar{V} \end{aligned}$$

The constant volume heat capacity is defined as:

$$\bar{C}_V = \left(\frac{\partial \bar{U}}{\partial T}\right)_V$$

We can rewrite this for internal energy:

$$d\bar{U} = \bar{C}_V dT$$

Combining these two expressions for internal energy, we obtain:

$$\bar{C}_V dT = -Pd\bar{V}$$

Using the ideal gas law for pressure of an ideal gas:

$$\bar{C}_V dT = -\frac{RT}{\bar{V}} d\bar{V}$$

Separating variables:

$$\frac{\bar{C}_V}{T} dT = -\frac{R}{\bar{V}} d\bar{V}$$

This is an expression for an ideal path along a reversible, adiabatic path that relates temperature to volume. To find our path along a PV surface for an ideal gas, we can start in TV surface and convert to a PV surface. Let's go from (T_1, V_1) to (T_2, V_2).

$$\int_{T1}^{T_2} \frac{\bar{C}_V}{T} dT = -\int_{\bar{V}_1}^{\bar{V}_2} \frac{R}{\bar{V}} d\bar{V}$$

$$\bar{C}_V \ln\left(\frac{T_2}{T_1}\right) = -R \ln\left(\frac{\bar{V}_2}{\bar{V}_1}\right) = R \ln\left(\frac{\bar{V}_1}{\bar{V}_2}\right)$$

$$\ln\left(\frac{T_2}{T_1}\right) = \frac{R}{\bar{C}_V} \ln\left(\frac{\bar{V}_1}{\bar{V}_2}\right)$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{\frac{R}{\bar{C}_V}}$$

We know that:

$$R = \bar{C}_P - \bar{C}_V$$

$$\frac{R}{\bar{C}_V} = \frac{\bar{C}_P - \bar{C}_V}{\bar{C}_V} = \frac{\bar{C}_P}{\bar{C}_V} - 1$$

$$\frac{R}{\bar{C}_V} = \gamma - 1$$

Therefore:

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{\gamma - 1}$$

This expression shows that volume and temperature are inversely related. That is, as the volume increase from V_1 to V_2, the temperature must decrease from T_1 to T_2.

3.7: Pressure-Volume Work

3.7.1: Enthalpy

An important point is that pressure-volume work $-PdV$ is only one kind of work. It is the important one for gases but for most other systems we are interested in other kinds of work (e.g. electrical work in a battery).

A good way to measure ΔU's is to make sure there are no work terms at all. If so:

$$\Delta U_{nowork} = q + w = q + 0 = q$$

However, this means that the $-PdV$ volume work term should also be zero and this implies we must keep volumes the same. That can actually be hard. Therefore we define at new state function ENTHALPY

$$H \equiv U + PV$$

(The $\equiv$ symbol is used to show that this equality is actually a definition.)

If we differentiate we get:

$$dH = dU + d(PV) = dU + PdV + VdP$$

We know that under reversible conditions we have

$$dU = \delta w + \delta q = -PdV + \delta q$$

(+ other work terms that we assume zero)

Thus,

$$dH = -PdV + \delta q + PdV + VdP$$

$$dH = \delta q + VdP$$

That means that as long as there is no other work and we keep the pressure constant:

$$\Delta H = q_P$$

instead of

$$\Delta U = q_V$$

Working at constant P is a lot easier to do than at constant V. This means that the enthalpy is a much easier state function to deal with than the energy U.

For example when we melt ice volumes change whether we like or not, but at long as the weather does not change too much pressure is constant. So if we measure how much heat we need to add to melt a mole of ice we get the molar heat of fusion:

Image:CH431 Image71.gif

Such enthalpies are measured and tabulated.

In this case the volume change is actually quite small, as it usually is for condensed matter. Only if we are dealing with gases is the difference between enthalpy and energy really important

So, U H for condensed matter, but U and H differ for gases.

A good example of this is the difference between the heat capacity at constant V and at constant P. For most materials there is not much of a difference, but for an ideal gas we have

$$C_p = C - V + nR$$

Needless to say that the heat capacity is a path function: it depends on what you keep constant.

3.8: Heat Capacity is a Path Function

3.8.1: Determining enthalpies from heat capacities.

The functions H and C_p are related by differentiation:

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

This means that we can:

1. measure C_p as a function of temperature
2. integrate this function and find $H(T)$

However, there are problems with this approach:

1. Reference point: we have to deal with the lower limit of integration.

    Ideally we start at zero Kelvin (but we cannot get there), but how do we compare one compound to the other?

2. At temperatures where there is a phase transition there is a sudden jump in enthalpy. E.g. when ice melts we have to first add the heat of fusion until all ice is gone before the temperature can go up again (assuming all is done under reversible well-equilibrated conditions).
3. At the jumps in H, the C_p is infinite.

> *It should be stressed that there* ***are no absolute enthalpies****.*

3.9: Relative Enthalpies Can Be Determined from Heat Capacity Data and Heats of Transition

It should be stressed that there **are no absolute enthalpies**. All that is properly defined are differences in enthalpy ΔH and these are only defined for ***processes***

When dealing with enthalpies

Define the Process

For example for the process of:

Process 1: ***heating ice from -20°C to -0°C***

We could write $\Delta H_1 = \int C_{P,ice}.\ dT$ from T=253K to T=273K = H(273) -H(253). But before moving beyond the melting point first a different process needs to take place, that of

Process 2: ***melting***

This gives us $\Delta_{fus}H = H_{liquid} - H_{solid}$ (both at 273K!). When we heat the liquid water further to say +20°C we would have to integrate over the heat capacity of the liquid.

Process 3: ***heating water from 0°C to +20°C***

We could write

$$\Delta H_3 = \int C_{P,water}\, dT$$

from T=273K to T=293K = H(293)-H(273).

The total change in enthalpy between -20 and +20 would be the sum of the three enthalpy changes.

$$\Delta H_{totalprocess} = \Delta H_1 + \Delta_{fus} H + \Delta H_3$$

Of course we could consider doing the same calculation for any temperature between -20 and +20 and summarize all our results in a graph. The three processes can thus schematically be shown in Figure 19.10.1 .

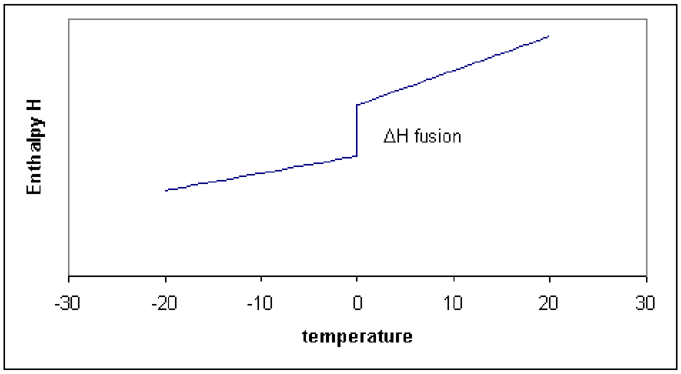


Figure 19.10.1 *: Schematic enthalpy function showing the jump at the melting point*

Notice that the slopes (i.e. the heat capacities!) before and after the melting point differ. The slope for the liquid is a little steeper because the liquid has more degrees of freedom and therefore the heat capacity of the liquid tends to be higher than of the solid. In the figure the enthlapy curves are shown as straight lines. This would be the case if the heat capacities are *constant* over the temperature interval. Although C_p is typically a 'slow' or 'weak' function of temperature it usually does change a bit, which means that the straight lines for H become curves.

> *Although C_p is typically a 'slow' or 'weak' function of temperature and is well approximated as a constant.*

Notice that for process two, the temperature is constant, that means that ΔT or dT is zero, but ΔH is finite, consequently ΔH/ΔT is infinitly large. Taking the limit for ΔT going to zero, we get a derivative:

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

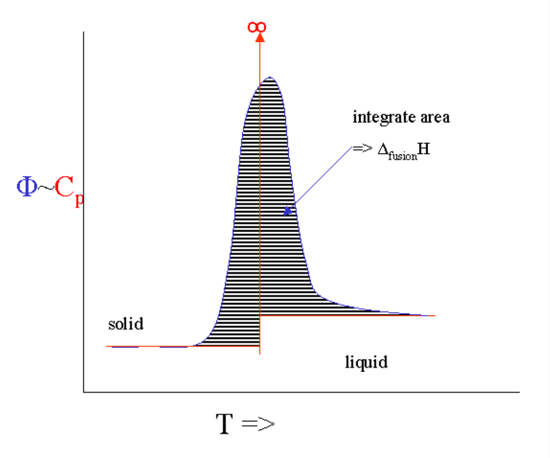
This derivative, the heat capacity must undergo a singularity: the slope is infinitely large (i.e, the H curve goes straight up). When there are more phase transitions, more discontinuities in H and singularities in C_p result (Figure 19.10.1). Note that $H(T) - H(0)$, not $H(T)$ is plotted to avoid the question what the absolute enthalpy is.

Scanningcalorimetry

There is technique that allows us to measure the heat capacity as a function of temperature fairly directly. It is called Differential Scanning Calorimetry (DSC). You put a sample in a little pan and put the pan plus an empty reference pan in the calorimeter. The instrument heats up both pans with a constant heating rate. Both pans get hotter by ***conduction***, but the heat capacity of the filled pan is obviously bigger. This means that the heat flow into the sample pan must be a bit bigger than into the empty one. This differential heat flow induces a tiny temperature difference ΔT between the two pans that can be measured. This temperature difference is proportional to the heat flow difference which is proportional to the heat capacity difference.

$$\Delta T \ \Delta \Phi \ \Delta_{betweenpans} C_p = C_p^{sample} \ (ifthepanscancel)$$

However, there are number of serious broadening issues with the technique. If you melt something you will never get to see the infinite singularity of the heat capacity. Instead it broadens out into a peak. If you integrate the peak you get the Δ_{fusion}H and the onset is calibrated to give you the melting point.



The ideal heat capacity signal and its broadened DSC signal

It is even possible to heat the sample with a rate that fluctuates with a little sine wave. This "Modulated DSC" version can even give you the (small) difference in C_p before and after the melting event.

3.10: Enthalpy Changes for Chemical Equations are Additive

3.10.1: Hess's law

As enthalpy and energy are state functions we should expect ***additivity*** of U and H when we study chemical reactions. This additivity is expressed in **Hess's Law**. The additivity has important consequences and the law finds wide spread application in the prediction of heats of reaction.

1. The reverse reaction has the negative enthalpy of the forward one.
2. If we can do a reaction in two steps we can calculate the enthalpy of the combined reaction by adding up:

Reaction	Enthalpy
$C_{(s)}$ + ½ $O_{2(g)}$ -> $CO_{(g)}$	Δ_rH = -110.5 kJ
$CO_{(g)}$ + ½ $O_{2(g)}$ -> $CO_{2(g)}$	Δ_rH = -283.0 kJ
This means that	---------------------+
$C_{(s)}$ + O2(g) -> CO2(g)	Δ_rH = -393.5 kJ

By this mechanism it is often possible to calculate the heat of a reaction even if this reaction is hard to carry out. E.g. we could burn both graphite and diamond and measure the heats of combustion for both. The difference would give us the heat of the transformation reaction from graphite to diamond.

3.10.1.1: Reaction-as-written convention (caution!)

The enthalpy is for the ***reaction-as-written***. That means that if we write:

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

with Δ_rH = -221 kJ (***not***: -110.5 kJ)

3.10.1.2: Reverse reactions

Because H is a state function the reverse reaction has the same enthalpy but with opposite sign

$$2CO(g) \rightarrow 2C(s) + O_2(g)$$

with Δ_rH = +221 kJ

3.10.1.3: Combining values

It is quite possible that you cannot really do a certain reaction in practice. For many reactions we can arrive at enthalpy values by doing some bookkeeping. For example, we can calculate the enthalpy for the reaction of PCl_3 with chlorine if we know the two reactions that the elements phosphorous and chlorine can undergo.

> *You do have to make sure you balance your equations properly!*

3.11: Heats of Reactions Can Be Calculated from Tabulated Heats of Formation

Reaction enthalpies are important, but difficult to tabulate. However, because enthalpy is a state function, it is possible to use **Hess' Law** to simplify the tabulation of reaction enthalpies. Hess' Law is based on the addition of reactions. By knowing the reaction enthalpy for constituent reactions, the enthalpy of a reaction that can be expressed as the sum of the constituent reactions can be calculated. The key lies in the canceling of reactants and products that °Ccur in the "data" reactions but not in the "target reaction.

Example 3.11.1:

Find ΔH_{rxn} for the reaction

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

Given

$$C(gr) + ½O_2(g) \rightarrow CO(g)$$

with $\Delta H_1 = -110.53\, kJ$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_2 = -393.51\, kJ$

Solution

The target reaction can be generated from the data reactions.

$$2\times [CO(g) \rightarrow C(gr) + O_2(g)]$$

plus

$$2\times [C(gr) + 2O_2(g) \rightarrow 2CO_2(g)]$$

equals

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

so

$$2\times\Delta H_1 = -787.02\, kJ$$

$$2\times\Delta H_2 = 221.06\, kJ$$

$$2\times\Delta H_1 + 2\times\Delta H_2 = -565.96\, kJ$$

3.11.1: Standard Enthalpy of Formation

One of the difficulties with many thermodynamic state variables (such as enthalpy) is that while it is possible to measure changes, it is impossible to measure an absolute value of the variable itself. In these cases, it is necessary to define a zero to the scale defining the variable. For enthalpy, the definition of a zero is that the standard enthalpy of formation of a pure element in its standard state is zero. All other enthalpy changes are defined relative to this standard. Thus it is essential to very carefully define a standard state.

Definition: the Standard State

The standard state of a substance is the most stable form of that substance at 1 atmosphere pressure and the specified temperature.

Using this definition, a convenient reaction for which enthalpies can be measured and tabulated is the **standard formation reaction**. This is a reaction which forms one mole of the substance of interest in its standard state from elements in their standard states. The enthalpy of a standard formation reaction is the **standard enthalpy of formation** (ΔH_{f^o}). Some examples are

- $NaCl(s)$:

  $$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$$

  with $\Delta H_f^o = -411.2\, kJ/mol$
- $C_3H_8(g)$:

  $$3C(gr) + 4H_2(g) \rightarrow C_3H_8(g)$$

  with $\Delta H_f^o = -103.8\, kJ/mol$

It is important to note that the standard state of a substance is **temperature dependent**. For example, the standard state of water at -10 °C is solid, whereas the standard state at room temperature is liquid. Once these values are tabulated, calculating reaction enthalpies becomes a snap. Consider the heat combustion (ΔH_c) of methane (at 25 °C) as an example.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

The reaction can expressed as a sum of a combination of the following standard formation reactions.

$$C(gr) + 2H_2(g) \rightarrow CH_4(g)$$

with $\Delta H_f^o = -74.6\, kJ/mol$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_f^o = -393.5\, kJ/mol$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$

with $\Delta H_f^o = -285.8\, kJ/mol$

The target reaction can be generated from the following combination of reactions

$$-1\times [C(gr) + 2H_2(g) \rightarrow CH_4(g)]$$

$$CH_4(g) \rightarrow C(gr) + 2H_2(g)$$

with $\Delta H_f^o = -1\times [-74.6\, kJ/mol] = 74.6\, kJ/mol$

$$C(gr) + O_2(g) \rightarrow CO_2(g)$$

with $\Delta H_f^o = -393.5\, kJ/mol$

$$2\times [H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)]$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

with $\Delta H_f^o = 2\times [-285.8\, kJ/mol] = -571.6\, kJ/mol.$

$$CH_4(g) + 2O_2(g) \rightarrow CO2_(g) + 2H_2O(l)$$

with $\Delta H_c^o = -890.5\, kJ/mol$

Alternately, the reaction enthalpy could be calculated from the following relationship

$$\Delta H_{rxn} = \sum_{products} \nu \cdot \Delta H_f^o - \sum_{reactants} \nu \cdot \Delta H_f^o$$

where ν is the stoichiometric coefficient of a species in the balanced chemical reaction. For the combustion of methane, this calculation is

$$\begin{aligned}
\Delta_{rxn} &= (1\, mol)\left(\Delta H_f^o(CO_2)\right) + (2\, mol)\left(\Delta H_f^o(H_2O)\right) - (1\, mol)\left(\Delta H_f^o(CH_4)\right) && (3.11.1)\\
&= (1\, mol)(-393.5\, kJ/mol) + (2\, mol)\,(-285.8\, kJ/mol) - (1\, mol)\,(-74.6\, kJ/mol) && (3.11.2)\\
&= -890.5\, kJ/mol && (3.11.3)
\end{aligned}$$

A note about units is in order. Note that reaction enthalpies have units of kJ, whereas enthalpies of formation have units of kJ/mol. The reason for the difference is that enthalpies of formation (or for that matter enthalpies of combustion, sublimation, vaporization, fusion, etc.) refer to specific substances and/or specific processes involving those substances. As such, the total enthalpy change is scaled by the amount of substance used. General reactions, on the other hand, have to be interpreted in a very specific way. When examining a reaction like the combustion of methane

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

with $\Delta H_{rxn} = -890.5\, kJ$. The correct interpretation is that the reaction of one mole of $CH_4(g)$ with two moles of $O_2(g)$ to form one mole of $CO_2(g)$ and two moles of $H_2O(l)$ releases 890.5 kJ at 25 °C.

3.11.2: Ionization Reactions

Ionized species appear throughout chemistry. The energy changes involved in the formation of ions can be measured and tabulated for several substances. In the case of the formation of positive ions, the enthalpy change to remove a single electron at 0 K is defined as the **ionization potential**.

$$M(g) \rightarrow M^+(g) + e^-$$

with $\Delta H(0K) \equiv 1^{st}\text{ ionization potential (IP)}$

The removal of subsequent electrons requires energies called the 2^{nd} Ionization potential, 3^{rd} ionization potential, and so on.

$$M^+(g) \rightarrow M^{2+}(g) + e^-$$

with $\Delta H(0K) \equiv 2^{nd} IP$

$$M^{2+}(g) \rightarrow M^{3+}(g) + e^-$$

with $\Delta H(0K) \equiv 3^{rd} IP$

An atom can have as many ionization potentials as it has electrons, although since very highly charged ions are rare, only the first few are important for most atoms.

Similarly, the **electron affinity** can be defined for the formation of negative ions. In this case, the first electron affinity is defined by

$$X(g) + e^- \rightarrow X^-(g)$$

with $-\Delta H(0K) \equiv 1^{st}\text{ electron affinity (EA)}$

The minus sign is included in the definition in order to make electron affinities mostly positive. Some atoms (such as noble gases) will have negative electron affinities since the formation of a negative ion is very unfavorable for these species. Just as in the case of ionization potentials, an atom can have several electron affinities.

$$X^-(g) + e^- \rightarrow X^{2-}(g)$$

with $-\Delta H(0K) \equiv 2^{nd} EA$.

$$X^{2-}(g) + e^- \rightarrow X^{3-}(g)$$

with $-\Delta H(0K) \equiv 3^{rd} EA$.

3.11.3: Average Bond Enthalpies

In the absence of standard formation enthalpies, reaction enthalpies can be estimated using average bond enthalpies. This method is not perfect, but it can be used to get ball-park estimates when more detailed data is not available. A **bond dissociation energy** D is defined by

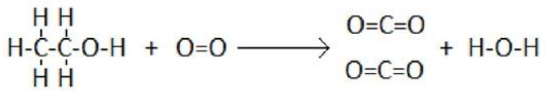
$$XY(g) \rightarrow X(g) + Y(g)$$

with $\Delta H \equiv D(X-Y)$

In this process, one adds energy to the reaction to break bonds, and extracts energy for the bonds that are formed.

$$\Delta H_{rxn} = \sum(\text{bonds broken}) - \sum(\text{bonds formed})$$

As an example, consider the combustion of ethanol:



In this reaction, five C-H bonds, one C-C bond, and one C-O bond, and one O=O bond must be broken. Also, four C=O bonds, and one O-H bond are formed.

Bond	Average Bond Energy (kJ/mol)
C-H	413
C-C	348
C-O	358
O=O	495
C=O	799
O-H	463

The reaction enthalpy is then given by

$$\begin{aligned} \Delta H_c &= 5(413\,kJ/mol) + 1(348\,kJ/mol) + 1(358\,kJ/mol) \\ &\quad + 1(495\,kJ/mol) - 4(799\,kJ/mol) - 2(463\,kJ/mol) \\ &= -856\,kJ/mol \end{aligned} \tag{3.11.4}$$

Because the bond energies are defined for gas-phase reactants and products, this method does not account for the enthalpy change of condensation to form liquids or solids, and so the result may be off systematically due to these differences. Also, since the bond enthalpies are averaged over a large number of molecules containing the particular type of bond, the results may deviate due to the variance in the actual bond enthalpy in the specific molecule under consideration. Typically, reaction enthalpies derived by this method are only reliable to within ± 5-10%.

3.12: The Temperature Dependence of ΔH

It is often required to know thermodynamic functions (such as enthalpy) at temperatures other than those available from tabulated data. Fortunately, the conversion to other temperatures is not difficult.

At constant pressure

$$dH = C_p\, dT$$

And so for a temperature change from T_1 to T_2

$$\Delta H = \int_{T_2}^{T_2} C_p\, dT \tag{3.12.1}$$

Equation 3.12.1 is often referred to as *Kirchhoff's Law*. If C_p is independent of temperature, then

$$\Delta H = C_p\, \Delta T \tag{3.12.2}$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral in Equation 3.12.1. A common *empirical* model used to fit heat capacities over broad temperature ranges is

$$C_p(T) = a + bT + \frac{c}{T^2} \tag{3.12.3}$$

After combining Equations 3.12.3 and 3.12.1, the enthalpy change for the temperature change can be found obtained by a simple integration

$$\Delta H = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2}\right) dT \tag{3.12.4}$$

Solving the definite integral yields

$$\Delta H = \left[aT + \frac{b}{2}T^2 - \frac{c}{T}\right]_{T_1}^{T_2} \tag{3.12.5}$$

$$= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{3.12.6}$$

This expression can then be used with experimentally determined values of a, b, and c, some of which are shown in the following table.

Table 3.12.1: *Empirical Parameters for the temperature dependence of* C_p

Substance	a (J mol^{-1} K^{-1})	b (J mol^{-1} K^{-2})	c (J mol^{-1} K)
C(gr)	16.86	4.77 x 10^{-3}	-8.54 x 10^{5}
CO_2(g)	44.22	8.79 x 10^{-3}	-8.62 x 10^{5}
H_2O(l)	75.29	0	0
N_2(g)	28.58	3.77 x 10^{-3}	-5.0 x 10^{4}
Pb(s)	22.13	1.172 x 10^{-2}	9.6 x 10^{4}

✓ Example 3.12.1: Heating Lead

What is the molar enthalpy change for a temperature increase from 273 K to 353 K for Pb(s)?

Solution

The enthalpy change is given by Equation 3.12.1 with a temperature dependence C_p given by Equation 3.12.1 using the parameters in Table 3.12.1. This results in the integral form (Equation 3.12.6):

$$\Delta H = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

when substituted with the relevant parameters of Pb(s) from Table $3.12.1$.

$$\begin{aligned}\Delta H = &(22.14\ \frac{J}{mol\ K}(353\ K - 273\ K)\\ &+\frac{1.172\times 10^{-2}\ \frac{J}{mol\ K^2}}{2}\left((353\ K)^2-(273\ K)^2\right)\\ &-9.6\times 10^4\ \frac{J\ K}{mol}\left(\frac{1}{(353\ K)}-\frac{1}{(273\ K)}\right)\\ \Delta H = &\ 1770.4\ \frac{J}{mol}+295.5\ \frac{J}{mol}+470.5\ \frac{J}{mol}\\ &=2534.4\ \frac{J}{mol}\end{aligned}$$

For chemical reactions, the reaction enthalpy at differing temperatures can be calculated from

$$\Delta H_{rxn}(T_2) = \Delta H_{rxn}(T_1) + \int_{T_1}^{T_2} \Delta C_p \Delta T$$

✓ Example 3.12.2: Enthalpy of Formation

The enthalpy of formation of NH_3(g) is -46.11 kJ/mol at 25 ^{o}C. Calculate the enthalpy of formation at 100 ^{o}C.

Solution

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

with $\Delta H\ (298\ K) = -46.11\ kJ/mol$

Compound	Cp (J mol^{-1} K^{-1})
N_2(g)	29.12
H_2(g)	28.82
NH_3(g)	35.06

$$\begin{aligned}\Delta H(373\ K) &= \Delta H(298\ K) + \Delta C_p \Delta T\\ &= -46110 + \frac{J}{mol}\left[2\left(35.06\frac{J}{mol\ K}\right)-\left(29.12\ \frac{J}{mol\ K}\right)-3\left(28.82\ \frac{J}{mol\ K}\right)\right](373\ K - 298\ K)\\ &= -49.5\ \frac{kJ}{mol}\end{aligned}$$

3.13: Enthalpy is a State Function

Our expression for internal energy at constant pressure:

$$\Delta U = q_P + w = q_P - P\Delta V$$

Rearrange:

$$q_P = \Delta U + P\Delta V = U_2 - U_1 + P(V_2 - V_1)$$

$$q_P = (U_2 + PV_2) - (U_1 + PV_1)$$

We can define this term as enthalpy:

$$H \equiv U + PV$$

This is a new state function.

3.E: The First Law of Thermodynamics (Exercises)

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{3.E.1}$$

You can see from Equation 3.E.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise $3.E.1$

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

CHAPTER OVERVIEW

4: Entropy and The Second Law of Thermodynamics

4.1: Energy Does not Determine Spontaneity

There are many spontaneous events in nature. If you open the valve in both cases a spontaneous event occurs. In the first case the gas fills the evacuated chamber, in the second the gases will mix. The state functions U and H do not give us a clue what will happen. You might think that only those events are spontaneous that produce heat.

Not so:

- If you dissolve $\mathrm{KNO_3}$ in water, it does so spontaneously, but the solution gets ***cold***.
- If you dissolve KOH in water, it does so spontaneously, but the solution gets ***hot***.

Clearly the first law is not enough to describe nature.

4.1.1: Two items left on our wish list

The development of the new state function entropy has brought us much closer to a complete understanding of how heat and work are related:

1. the spontaneity problem

    we now have a criterion for spontaneity for isolated systems

2. the asymmetry between work->heat (dissipation) and heat->work (power generation)

    at least we can use the new state law to predict the limitations on the latter.

Two problems remain:

1. we would like a spontaneity criterion *for all systems* (not just isolated ones)
2. we have a new state function S, but what is it?

4.1.2: Entropy on a microscopic scale

Let us start with the latter. Yes we can use S to explain the odd paradox between w and q both being forms energy on the one hand, but the conversion being easier in one direction than the other, but we have introduced the concept *entropy* purely as a phenomenon on iis own. Scientifically there is nothing wrong with such a phenomenological theory except that experience tells us that if you can understand the phenomenon itself better your theory becomes more powerful.

To understand entropy better we need to leave the macroscopic world and look at what happens on a molecular level and do statistics over many molecules. First, let us do a bit more statistics of the kind we will need.

4.1.2.1: Permutations

If we have n distinguishable objects, say playing cards we can arrange them in a large number of ways. For the first object in our series we have n choices, for number two we have $n-1$ choices (the first one being spoken for) etc. This means that in total we have

$$W = n(n-1)(n-2)\ldots.4.3.2.1 = n! \text{ choices.}$$

The quantity W is usually called the number of realizations in thermodynamics.

The above is true if the objects are all distinguishable. If they fall in groups within which they are not distinguishable we have to correct for all the swaps within these groups that do not produce a distinguishably new arrangement. This means that W becomes $\frac{n!}{a!b!c!\ldots z!}$ where a,b, c to z stands for the size of the groups. (Obviously $a+b+c+..+z=n$)

In thermodynamincs our 'group of objects' is typically an ensemble of systems, think of size N_{av} and so the factorial become horribly large. This makes it necessary to work with logarithms. Fortunately there is a good approximation (by Stirling) for a logarithmic factorial:

$$\ln N! \approx N \ln N - N$$

Causality vs. Correlation

In Europe nosey little children who are curious to find out where their newborn little brother or sister came from, often get told that the stork brought it during the night. When you look at the number of breeding pairs of this beautiful bird in e.g. Germany since 1960 you see a long decline to about 1980 when the bird almost got extinct. After that the numbers go up again due to breeding programs mostly. The human birth rate in the country follows a pretty much identical curve and the correlation between the two is very high (>0.98 or so). (Dr H. Sies in Nature (volume 332 page 495; 1988). Does this prove that storks indeed bring babies?

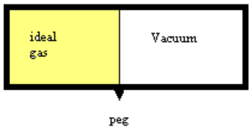
An adult White Stork. from Wikipedia (credit: Frank Vassen).

Answer:

No, it does ***not*** show causality, just a correlation due a common underlying factor. In this case that is the choices made by the German people. First they concentrated on working real hard and having few children to get themselves out of the poverty WWII had left behind and neglected the environment, then they turned to protect the environment and opened the doors to immigration of people, mostly from Muslim countries like Turkey or Morocco, that usually have larger families. The lesson from this is that you can only conclude causality ***if*** you are sure that there are no other intervening factors.

4.1.3: Changing the size of the box with the particles in it

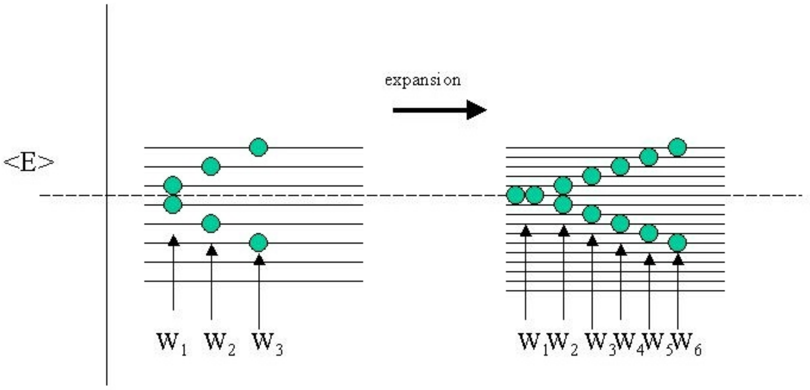
The expansion of an ideal gas against vacuum is really a wonderful *model experiment*, because *nothing else happens* but a spontaneous expansion and a change in entropy. No energy change, no heat, no work, no change in mass, no interactions, nothing. In fact, it does not even matter whether we consider it an isolated process or not. We might as well do so.



Physicists and Physical Chemists love to find such experiments that allows them to retrace *causality*. All this means that if we look at what happens at the atomic level, we should be able to retrace the ***cause*** of the entropy change. As we have seen before, the available energy states of particles in a box depend on the size of the box.

$$E_{kin} = \frac{h^2}{8ma^2}\left[n_1^2 + n_2^2 + n_2^2\right]$$

Clearly if the side (a and therefore the volume of the box changes, the energy spacing between the states will become smaller. Therefore during our expansion against vacuum, the energy states inside the box are changing. Because U does not change the *average* energy $\langle E\rangle$ is constant. Of course this average is taken over a great number of molecules (*systems*) in the gas (the *ensemble*), but let's look at just two of them and for simplicity let us assume that the energy of the states are equidistant (rather than quadratic in the quantum numbers n).



As you can see there is more than one way to skin a cat, or in this case to *realize* the same average $\langle E\rangle$ of the complete ensemble (of only two particles admittedly). Before expansion I have shown three realizations W_1, W_2, W_3 that add up to the same $\langle E\rangle$. After expansion however, there are more energy states available and the schematic figure shows twice as many realizations W in the same energy interval.

Boltzmann was the first to postulate that this is what is at the root of the entropy function, not so much the (total) energy itself (that stays the same!), but the number of ways the energy can be distributed in the ensemble. Note that because the ensemble average (or total) energy is identical, we could also say that the various realizations W represent the degree of *degeneracy* Ω of the ensemble.

Boltzmann considered a much larger (*canonical*) ensemble consisting of a great number of identical *systems* (e.g. molecules, but it could also be planets or so). If each of our systems already has a large number of energy states the systems can all have the same (total) energy but distributed in rather different ways. This means that two systems within the ensemble can either have the same distribution or a different one. Thus we can divide the ensemble A in subgroups a_j having the same energy distribution and calculate the number of ways to distribute energy in the ensemble A as

$$W = \frac{A!}{a1!a2!\ldots}.$$

Boltzmann postulated that entropy was directly related to the number of realizations W, that is the number of ways the same energy can be distributed in the ensemble. This leads immediately to the concept of order versus disorder, e.g, if the number of realizations is $W = 1$, all systems must be in the same state (W=A! / A!0!0!0!…) which is a very orderly arrangement of energies.

If we were to add two ensembles to each other the total number of possible arrangements W_{tot} becomes the product W_1W_2 but the entropies should be additive. As logarithms transform products into additions Boltzmann assumed that the relation between W and S should be logarithmic and wrote:

$$S = k \ln W$$

Again, if we consider a very ordered state, e.g. where all systems are in the ground state the number of realizations A!/A!= 1 so that the entropy is zero. If we have a very messy system where the number of ways to distribute energy over the many many different states is very large S becomes very large. Thus entropy is very large.

This immediately gives us the driving force for the expansion of a gas into vacuum or the mixing of two gases. We simply get more energy states to play with, this increases W. This means an increase in S. This leads to a spontaneous process.

4.2: Nonequilibrium Isolated Systems Evolve in a Direction That Increases Their Energy Dispersal

In spontaneous processes for an isolated system, there is a competition between minimizing the energy of the system and increasing the dispersal of energy within the system. If energy is constant, then the system will evolve to maximize energy dispersal. If energy dispersal is not a factor, the system will evolve to minimize its energy. We already have a quantitative basis for the energy of a system and we need to do the same for energy dispersal. Suppose we have a small reversible change dU in the energy of an ideal gas. We know that U only depends on temperature:

$$dU = C_v dT$$

We also know that any reversible work would be volume work.

$$\delta w_{rev} = -PdV$$

This means that we can write:

$$\begin{aligned} \delta q_{rev} &= dU - \delta w_{rev} \\ &= C_v dT + PdV \end{aligned}$$

Let us examine if this represents an **exact differential**. If δq were an exact differential, we could write the total differential:

$$\delta q_{rev} = \left(\frac{\partial q}{dT}\right)_V dT + \left(\frac{\partial q}{dV}\right)_T dV$$

And the following would be true:

$$\frac{\partial^2 q_{rev}}{\partial T \partial V} = \frac{\partial^2 q_{rev}}{\partial V \partial T}$$

From our equation above, we know that:

$$\frac{\partial q_{rev}}{\partial T} = C_V$$

$$\frac{\partial q_{rev}}{\partial V} = P$$

Therefore, the following should be true:

$$\frac{\partial C_V}{\partial V} = \frac{\partial P}{\partial T}$$

However,

$$\frac{\partial C_v}{\partial V} = 0$$

Because C_v does not depend on volume (only T, just like U: it is its derivative). And:

$$\frac{\partial P}{\partial T} = \frac{\partial nRT}{\partial T} = \frac{nR}{V}$$

Which is not zero!! Clearly, δq_{rev} is **not a state function**, but look what happens if we multiply everything with an 'integration factor' $1/T$:

$$\frac{\delta q_{rev}}{T} = \frac{C_v}{T} dT + \frac{P}{T} dV$$

$$\frac{\partial C_v/T}{\partial V} = 0$$

Because $\frac{C_v}{T}$ does not depend on volume. However,

$$\frac{\partial(P/T)}{\partial T}=\frac{\partial(nR/V)}{\partial T}=0$$

Thus, the quantity $dS=\frac{\delta q_{rev}}{T}$ is an exact differential, so S is a state function and it is called **entropy**. Entropy is the dispersal of energy, or equivalently, the measure of the number of possible microstates of a system.

4.3: Unlike heat, Entropy is a State Function

4.3.1: Circular integrals

Because entropy is a state function, it integrates to zero over any circular path going back to initial conditions, just like U and H:

$$\oint dS = 0$$

$$\oint dH = 0$$

$$\oint dU = 0$$

As discussed previously, we can use this fact to revisit the isotherm + isochore + adiabat circular path (Figure 20.3.1).

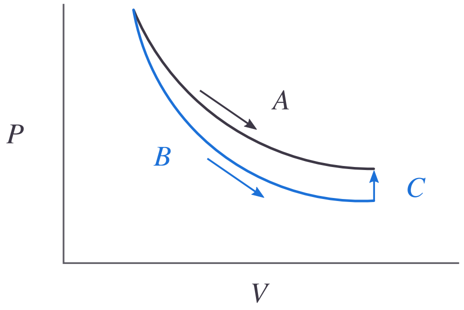


Figure 20.3.1 : A: isothermal expansion, B:adiabat, C:isochore (CC BY-NC; Ümit Kaya via LibreTexts)

Along adiabat B and isochore C:

- There is no heat transfer along adiabat B:

$$q_{rev,B} = 0$$

- There is no work along isochore C:

$$\delta w = 0$$

- But the temperature changes from T_2 back to T_1. This requires heat:

$$q_{rev,C} = C_V \Delta T$$

Along the isotherm A:

- We have seen that

$$q_{rev,A} = nRT \ln \frac{V_2}{V_1}$$

The quantities $q_{rev,A}$, $q_{rev,B}$, and $q_{rev,C}$ are ***not*** the same, which once again underlines that heat is a path function. How about entropy?

First, consider the combined paths of B and C:

$$q_{rev,B+C} = \int_{T_2}^{T_1} C_v dT$$

$$\int dS_{B+C} = \int \frac{dq_{rev,B+C}}{T} = \int_{T_2}^{T_1} \frac{C_v}{T} dT$$

We had seen this integral before from Section 19-6, albeit from T_1 to T_2:

$$\Delta S_{B+C}=nR\ln\frac{V_2}{V_1} \tag{4.3.1}$$

(Notice sign in Equation 4.3.1 is positive)

Along the isotherm A:

$$q_{rev,A}=nRT\ln\frac{V_2}{V_1}$$

T is a constant so we can just divide $q_{rec,A}$ by T to get ΔS_A:

$$\Delta S_A=nR\ln\frac{V_2}{V_1}$$

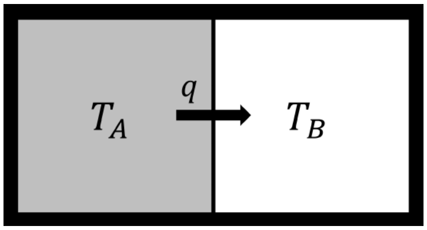
We took two different paths to get start and end at the same points. Both paths had the same change in entropy. Clearly entropy is a *state function* while q_{rev} is not.

4.4: The Second Law of Thermodynamics

4.4.1: Spontaneity of an isolated system

> An **isolated system** is a little more than just adiabatic. In the latter heat cannot get in or out. In an isolated system *nothing* gets in or out, neither heat nor mass nor even any radiation, such as light. The isolated system is like a little universe all to itself.

Let us consider a zero law process. We have two identical blocks of metal, say aluminum. They are each at thermal equilibrium, but at different temperatures. They are brought into contact with each other but isolated from the rest of the universe.



- ***Zeroth law***: *Heat will flow from hot to cold*
- ***First law***: *There is no change in total energy*

so:

$$dU_A = -dU_B$$

There is also no work so:

$$dU_A = \delta q_A + 0$$

Because U is a state function this makes q a state function as well, otherwise this equality does not hold. As there is only one term on the right there is only one path (along q). So we could write:

$$dU_A = dq_A$$

This implies that we do not need to worry about reversible and irreversible paths as there is only one path. Since:

$$dS = \frac{\delta q_{rev}}{T}$$

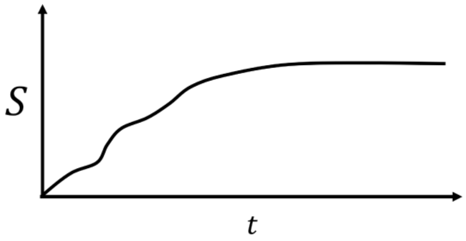
In this particular case:

$$TdS = \delta q_{rev} = dU$$

Thus we get:

$$dS = \frac{dU_A}{T_A} + \frac{dU_B}{T_B} = \frac{dU_A}{T_A} - \frac{dU_A}{T_B} = dU_A\left(\frac{1}{T_A} - \frac{1}{T_B}\right)$$

Clearly as long as the two temperatures are not the same dS is not zero and entropy is not conserved. Instead it is **increasing**. Over time, the temperatures will become the same (if the blocks are identical, the final temperature is the average of T_A and T_B) and the entropy will reach a maximum.



For our two identical blocks of metal (with same heat capacity, C_V), we can, in fact, derive that the entropy change:

$$\Delta S = C_V \ln\left[\frac{T_A^2 + T_B^2}{4T_A T_B}\right].$$

This is indeed a positive quantity. In general, we can say for an isolated system:

$$dS \geq 0$$

Thus if we are dealing with a spontaneous (and isolated) process $dS > 0$ and ***entropy is being produced***. This gives us a ***criterion for spontaneity***.

4.4.2: Entropy exchange of an open system

In an isolated system dS represents the produced entropy dS_{prod} and this is a good criterion for spontaneity. Of course the requirement that the system is isolated is very restrictive and makes the criterion as good as useless... What happens in a system that can exchange heat with the rest of the universe? We do have entropy changes in that case, but part of them may have nothing to do with production, because we also have to consider the heat that is exchanged.

$$dS = dS_{prod} + dS_{exchange}$$

If the process is reversible (that is completely non-spontaneous) we are dealing with δq_{rev} so that $dS_{exchange} = \delta q_{rev}/T$, but that is also what dS_{tot} is equal to (by definition). This leaves no room for entropy production.

So we have:

Isolated: $dS = dS_{prod} + 0$

Reversible $dS = 0 + \delta q_{rev}/T$

Notice that this demonstrates that for non-isolated systems entropy change is *not* a good criterion for spontaneity at all... In the case the heat exchange is ***irreversible*** *part* of the entropy is entropy production by the system:

Irreversible: $dS = dS_{prod} + \delta q_{irrev}/T$

$dS > \delta q_{irrev}/T$ in this case.

Generalizing the isolated, irreversible and reversible cases we may say:

$$dS \geq \frac{\delta q}{T}$$

This is the ***Clausius inequality***.

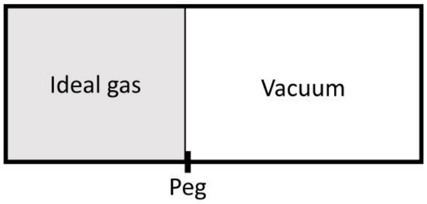
4.5: We Must Always Devise a Reversible Process to Calculate Entropy Changes

The second law of thermodynamics can be formulated in many ways, but in one way or another they are all related to the fact that the state function entropy, S, tends to increase over time in isolated systems. For a long time, people have looked at the entire universe as an example of an isolated system and concluded that its entropy must be steadily increasing until $\delta S_{universe}$ becomes zero. As we will see below, the second law has important consequences for the question of how we can use heat to do useful work.

> Of late, cosmologists like the late Richard Hawkins have begun to question the assumption that the entropy of the universe is steadily increasing. The key problem is the role that gravity and relativity play in creating black holes.

4.5.1: Vacuum Expansion

Let's compare two expansions from V_1 to V_2 for an ideal gas, both are isothermal. The first is an irreversible one, where we pull a peg an let the piston move against vacuum:



The second one is a reversible isothermal expansion from V_1 to V_2 (and P_1 to P_2) that we have examined before. In both cases, the is no change in internal energy since T does not change. During the irreversible expansion, however, there is also no volume work because the piston is expanding against a vacuum and the following integral:

$$\int -P_{ext}\, dV = 0$$

integrates to zero. The piston has nothing to perform work against until it slams into the right hand wall. At this point $V = V_2$ and then dV becomes zero. This is not true for the reversible isothermal expansion as the external pressure must always equal the internal pressure.

> *No energy and no work means no heat!*

Clearly the zero heat is irreversible heat ($q_{irr} = 0$) and this makes it hard to calculate the entropy of this spontaneous process. But then this process ends in the same final state as the reversible expansion from V_1 to V_2. We know that dU is still zero, but now $\delta w_{rev} = -\delta q_{rev}$ is nonzero. We calculated its value before:

$$q_{rev} = nRT \ln\left(\frac{V_2}{V_1}\right) \tag{4.5.1}$$

The Claussius definition of entropy change can be used to find ΔS (under constant temperature).

$$\Delta S = \frac{q_{rev}}{T} \tag{4.5.2}$$

Substituting Equation 4.5.1 into Equation 4.5.2 results in

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$$

As S is a state function this equation also holds for the irreversible expansion against vacuum.

> Always calculate the entropy difference between two points along a **reversible** path.

For the irreversible expansion into vacuum we see that

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= nR\ln\left(\frac{V_2}{V_1}\right) + 0 \\ &= nR\ln\left(\frac{V_2}{V_1}\right)\end{aligned}$$

For the reversible expansion, heat is transferred to the system while the system does work on the surroundings in order to keep the process isothermal:

$$\Delta S_{\text{sys}} = nR\ln\left(\frac{V_2}{V_1}\right)$$

The entropy change for the surrounding is the opposite of the system:

$$\Delta S_{\text{surr}} = -nR\ln\left(\frac{V_2}{V_1}\right)$$

This is because the amount of heat transferred to the system is the same as the heat transferred from the surroundings and this process is reversible so the system and surroundings are at the same temperature (equilibrium). Heat is related to entropy by the following equation:

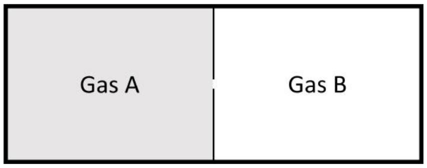
$$dS = \frac{\delta q}{T} \tag{4.5.3}$$

Therefore, the total entropy change for the reversible process is zero:

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= nR\ln\left(\frac{V_2}{V_1}\right) - nR\ln\left(\frac{V_2}{V_1}\right) \\ &= 0\end{aligned}$$

4.5.2: The Mixing of Two Gases

Consider two ideal gases at same pressure separated by a thin wall that is punctured. Both gases behave as if the other one is not there and again we get a spontaneous process, mixing in this case.



If the pressure is the same the number of moles of each gas should be proportional to the original volumes, V_A and V_B, and the total number of moles to the total volume V_{tot}.

For gas A we can write:

$$\Delta S_A = n_A R\ln\frac{V_{tot}}{V_A} = n_A R\ln\frac{n_{tot}}{n_A}$$

and similarly for gas B we can write:

$$\Delta S_B = n_B R\ln\frac{V_{tot}}{V_B} = n_B R\ln\frac{n_{tot}}{n_B}$$

The total entropy change is therefore the sum of constituent entropy changes:

$$\Delta S = \Delta S_A + \Delta S_B$$

and the entropy change total per mole of gas is:

$$\frac{\Delta S}{n_{tot}} = R \frac{\left[n_B \ln \frac{n_{tot}}{n_B} + n_A \ln \frac{n_{tot}}{n_A} \right]}{n_{tot}} \tag{4.5.4}$$

Equation 4.5.4 can be simplified using mole fractions:

$$\chi_A = \frac{n_A}{n_{tot}}$$

and the mathematical relationship of logarithms that:

$$\ln\left(\frac{x}{y}\right) = -\ln\left(\frac{y}{x}\right)$$

to:

$$\Delta \bar{S} = -R\left[\chi_A \ln \chi_A + \chi_B \ln \chi_B\right] \tag{4.5.5}$$

In the case of mixing of more than two gases, Equation 4.5.5 can be expressed as:

$$\Delta \bar{S} = -R \sum \chi_i \ln \chi_i \tag{4.5.6}$$

This entropy expressed in Equations 4.5.5 and 4.5.6 is known as the **entropy of mixing**; its existence is the major reason why there is such a thing as diffusion and mixing when gases, and also solutions (even solid ones), are brought into contact with each other.

4.E: Entropy and The Second Law of Thermodynamics (Exercises)

CHAPTER OVERVIEW

5: Entropy and the Third Law of Thermodynamics

5.1: Entropy Increases With Increasing Temperature

Learning Objectives

- Define entropy and its relation to energy flow.

5.1.1: Entropy versus temperature

We can put together the first and the second law for a reversible process with no other work than volume (PV) work and obtain:

$$dU = \delta q_{rev} + \delta w_{rev}$$

Entropy is the dispersal of energy and is related to heat:

$$\delta q_{rev} = TdS$$

Work is related to the change in volume:

$$\delta w_{rev} = -PdV$$

Plugging these into our expression for dU for reversible changes:

$$dU = TdS - PdV$$

We no longer have any path functions in the expression, as U, S and V are ***all state functions***. This means this expression must be an exact differential. We can generalize the expression to hold for irreversible processes, but then the expression becomes an inequality:

$$dU \leq TdS - PdV$$

This equality expresses U as a function of two variables, entropy and volume: $U(S,V)$. S and V are the ***natural variables*** of U.

5.1.1.1: Entropy and heat capacity

At constant volume, dU becomes:

$$dU = TdS$$

Recall that internal energy is related to constant volume heat capacity, C_V:

$$C_V = \left(\frac{dU}{dT}\right)_V$$

Combining these two expressions, we obtain:

$$dS = \frac{C_V}{T} dT$$

Integrating:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT$$

If we know how C_V changes with temperature, we can calculate the change in entropy, ΔS. Since heat capacity is always a positive value, entropy must increase as the temperature increases. There is nothing to stop us from expressing U in ***other*** variables, e.g. T and V. In fact, we can derive some interesting relationships if we do.

Example 21.1.1

1. Write U as a function of T and V.
2. Write U as a function of its natural variables.
3. Rearrange (2) to find an expression for dS.
4. Substitute (1) into (3) and rearrange. This is the definition of C_V.

5. Write out S as a function of T and V.

We can also derive an expression for the change in entropy as a function of constant pressure heat capacity, C_P. To start, we need to change from internal energy, U, to enthalpy, H:

$$\begin{aligned} H &= U + PV \\ dH &= dU + d(PV) \\ &= dU + PdV + VdP \end{aligned}$$

For reversible processes:

$$\begin{aligned} dH &= dU + PdV + VdP \\ &= TdS - PdV + PdV + VP \\ &= TdS + VdP \end{aligned}$$

The natural variables of the enthalpy are S and P (not: V). A similar derivation as above shows that the temperature change of entropy is related to the constant pressure heat capacity:

$$dH = TdS + VdP$$

At constant pressure:

$$dH = TdS + VdP$$

Recall that:

$$C_P = \frac{dH}{dT}$$

Combining, we obtain:

$$dS = \frac{C_P}{T} dT$$

Integrating:

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P(T)}{T} dT$$

This means that if we know the heat capacities as a function of temperature we can calculate how the entropy changes with temperature. Usually it is easier to obtain data under constant P conditions than for constant V, so that the route with C_p is the more common one.

5.2: The 3rd Law of Thermodynamics Puts Entropy on an Absolute Scale

In the unlikely case that we have C_p data all the way from 0 K we could write:

$$S(T) = S(0) + \int_0^T C_p dT$$

It is tempting to set the $S(0)$ to zero and make the entropy thus an absolute quantity. As we have seen with enthalpy, it was not really possible set $H(0)$ to zero. All we did was define ΔH for a particular process, although if C_p data are available we could construct an enthalpy function (albeit with a floating zero point) by integration of C_P (instead of C_p/T!).

Still for entropy S the situation is a bit different than for H. Here we can actually put things on an ***absolute*** scale. Both Nernst and Planck have proposed to do so. Nernst postulated that for a pure and perfect crystal S should indeed to go to zero as T goes to zero. For example, sulfur has two solid crystal structure, rhombic and monoclinic. At 368.5 K, the entropy of the phase transition from rhombic to monoclinic, $S_{(rh)} \rightarrow S_{(mono)}$, is:

$$\Delta_{\text{trs}} S(368.5 \text{ K}) = 1.09 \ \frac{\text{J} \cdot \text{mol}}{\text{K}}$$

As the temperature is lowered to 0 K, the entropy of the phase transition approaches zero:

$$\lim_{T \to 0} \Delta_r S = 0$$

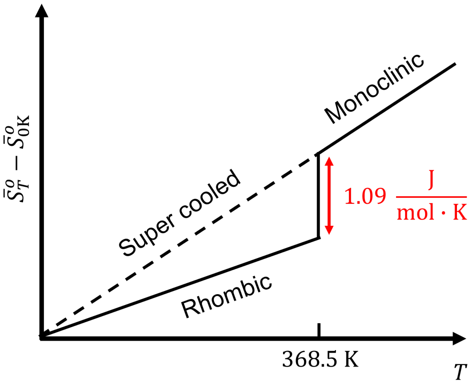


Figure 1. Schematic showing the entropy of the rhombic and monoclinic structures of sulfur as a function of temperature.

This shows that the entropy of the two crystalline forms are the same. The only way is if all species have the same absolute entropy at 0 K. For energy dispersal at 0 K:

1. Energy is as concentrated as it can be.
2. Only the very lowest energy states can be occupied.

For a pure, perfect crystalline solid at 0 K, there is only one energetic arrangement to represent its lowest energy state. We can use this to define a natural zero, giving entropy an absolute scale. The **third Law of Thermodynamics** states that the entropy of a pure substance in a perfect crystalline form is 0 $\frac{\text{J}}{\text{mol} \cdot \text{K}}$ at 0 K:

$$\bar{S}^\circ_{0\text{ K}} = 0$$

This is consistent with our molecular formula for entropy:

$$S = k \ln W$$

For a perfect crystal at 0 K, the number of ways the total energy of a system can be distributed is one ($W = 1$). The $\ln W$ term goes to zero, resulting in the perfect crystal at 0 K having zero entropy.

It is certainly true that for the great majority of materials we end up with a crystalline material at sufficiently low materials (although there are odd exceptions like liquid helium). However, it should be mentioned that a completely *perfect* crystal can only be grown at zero Kelvin! It is not possible to grow anything at 0 K however. At any finite temperature the crystal always incorporates defects, more so if grown at higher temperatures. When cooled down very slowly the defects tend to be ejected from the lattice for the crystal to reach a new equilibrium with less defects. This tendency towards less and less disorder upon cooling is what the third law is all about.

However, the ordering process often becomes impossibly slow, certainly when approaching absolute zero. This means that real crystals always have *some* frozen in imperfections. Thus there is always *some* residual entropy. Fortunately, the effect is often too small to be measured. This is what allows us to ignore it in many cases (but not all).

We could state the Third law of thermodynamics as follows:

> *The entropy of a perfect crystal approaches zero when T approaches zero (but perfect crystals do not exist).*

Another complication arises when the system undergoes a phase transition, e.g. the melting of ice. As we can write:

$$\Delta_{fus} H = q_P$$

If ice and water are in equilibrium with each other the process is quite reversible and so we have:

$$\Delta_{fus} S = \frac{q_{rev}}{T} = \frac{\Delta_{fus} H}{T}$$

This means that at the melting point the curve for S makes a sudden jump by this amount because all this happens at one an the same temperature. Entropies are typically calculated from calorimetric data (C_P measurements e.g.) and tabulated in standard molar form. The standard state at any temperature is the hypothetical corresponding ideal gas at one bar for gases.

In table 21.3 a number of such values are shown. There are some clear trends. E.g. when the noble gas gets heavier this induces more entropy. This is a direct consequence of the particle in the box formula: It has mass in the denominator and therefore the energy levels get more crowded together when m increases: more energy levels, more entropy.

> *The energy levels get more crowded together when m increases: more energy levels, more entropy*

5.2.1: Tabulation of H, S and G. Frozen entropy

There are tables for $H^\circ(T) - H^\circ(0)$, $S^\circ(T)$ and $G^\circ(T) - H^\circ(0)$ as a function of temperature for numerous substances. As we discussed before the plimsoll defines are standard state in terms of pressure (1 bar) and of concentration reference states, if applicable, but temperature is the one of interest.

For most substances the Third Law assumption that $\lim S^\circ(T)$ for $T \rightarrow 0 = 0$ is a reasonable one but there are notable exceptions, such as carbon monoxide. In the solid form, carbon monoxide molecules should ideally be fully ordered at absolute zero, but because the sizes of the carbon atoms and the oxygen atoms are very close and the dipole of the molecule is small, it is quite possible to put in a molecule 'upside down', i.e. with the oxygen on a carbon site and vice versa. At higher temperatures, at which the crystal is formed, this lowers the Gibbs energy (G) because it increases entropy. In fact we could say that if we could put each molecule into the lattice in two different ways, the number of ways $W_{disorder}$ we can put N molecules in into the lattice is 2^N. This leads to an additional contribution to the entropy of

$$S_{disorder} = k \ln W_{disorder} = Nk \ln 2 = R \ln 2 = 5.7 \, \frac{\text{J}}{\text{mol} \cdot \text{K}})$$

Although at lower temperatures the entropy term in $G = H - TS$ becomes less and less significant and the ordering of the crystal to a state of lower entropy should become a spontaneous process, in reality the kinetics are so slow that the ordering process does not happen and solid CO therefore has a non-zero entropy when approaching 0 K.

In principle *all* crystalline materials have this effect to some extent, but CO is unusual because the concentration of 'wrongly aligned' entities is of the order of 50% rather than say 1 in 10^{13} (a typical defect concentration in say single crystal silicon).

5.3: The Entropy of a Phase Transition can be Calculated from the Enthalpy of the Phase Transition

Phase transitions (e.g. melting) often occur under equilibrium conditions. We have seen that both the H and the S curves undergo a discontinuity at constant temperature during melting, because there is an enthalpy of fusion to overcome. For a general phase transition at equilibrium at constant T and P, we can say that:

$$\Delta_{trs} G = \Delta_{trs} H - T_{trs} \Delta_{trs} S = 0$$

$$\Delta_{trs} H = T_{trs} \Delta_{trs} S$$

$$\frac{\Delta_{trs} H}{T_{trs}} = \Delta_{trs} S$$

For melting of a crystalline solid, we now see *why* there is a sudden jump in enthalpy. The reason is that the solid has a much more ordered structure than the crystalline solid. The decrease in order implies a finite $\Delta_{trs} S$. We should stress at this point that we are talking about ***first order*** transitions here. The reason for this terminology is that the discontinuity is in a function like S, that is a first order derivative of G (or A):

$$\left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}$$

Second order derivatives (e.g. the heat capacity) will display a singularity (+∞) at the transition point.

Every phase transition will have a change in entropy associated with it. The different types of phase transitions that can occur are:

$l \rightarrow g$	Vaporization / boiling
$g \rightarrow l$	Condensation
$s \rightarrow l$	Fusion / melting
$l \rightarrow s$	Freezing
$s \rightarrow g$	Sublimation
$g \rightarrow s$	Deposition
$s \rightarrow s$	Solid to solid phase transition

5.4: Standard Entropies Can Be Used to Calculate Entropy Changes of Chemical Reactions

Entropy is a state function, so we can calculate values for a process using any path. This allows us to calculate the entropy change of a chemical reaction using standard entropies. Specifically, we sum the entropies of the products and subtract the entropies of the reactions:

$$\Delta_{rxn} S^{\circ} = \sum_{\text{Products}} v_i S_i^{\circ} - \sum_{\text{Reactants}} v_i S_i^{\circ}$$

Where v_i is the stoichiometric coefficient. Let's look at the combustion of methane:

$$\mathrm{CH_4}\,(g) + 2\mathrm{O_2}\,(g) \rightarrow 2\mathrm{H_2O} + \mathrm{CO_2}\,(g)$$

The standard entropies are:

Molecule	Entropy $\left(\frac{\mathrm{J}}{\mathrm{mol \cdot K}}\right)$
$\mathrm{CH_4}$	186.25[1]
$\mathrm{O_2}$	205.15[1]
$\mathrm{H_2O}$	188.84[1]
$\mathrm{CO_2}$	213.79[1]

The entropy for the combustion of methane is:

$$\Delta S^{\circ} = [2\,(188.84) + 1\,(213.70)] - [1\,(186.25) + 2\,(205.15)] = -5.17\ \frac{\mathrm{J}}{\mathrm{mol \cdot K}}$$

5.4.1: References

1. Chase, M.W., Jr., *NIST-JANAF Themochemical Tables, Fourth Edition*, **J. Phys. Chem. Ref. Data, Monograph 9**, 1998, 1-1951.

5.E: Entropy and the Third Law of Thermodynamics (Exercises)

5.E.0.1: Problem 1

Liquid water has a nearly constant molar heat capacity of $\bar{C}_P = 75.4.\ \mathrm{J \cdot mol^{-1} K^{-1}}$. What is the change in entropy as 200. g of water are cooled from 70.0°C to 20.0°C?

CHAPTER OVERVIEW

6: Helmholtz and Gibbs Energies

6.1: Gibbs Energy Determines the Direction of Spontaneity at Constant Pressure and Temperature

The Helmholtz energy A is developed for isochoric changes and as we have often said before it is much easier to deal with isobaric ones where $P =$ constant. We can therefore repeat the above treatment for the enthalpy and introduce another state function the Gibbs energy

$$\begin{aligned} G &\equiv H - TS \\ &= U + PV - TS \\ &= A + PV \end{aligned}$$

If we take both T and P constant we get

$$dU - TdS + PdV \leq 0$$

$$dG \leq 0$$

G either decreases (spontaneously) or is constant (at equilibrium). Calculating the state function between two end points we get:

$$\Delta G = \Delta H - T\Delta S \leq 0 (T, P \text{ constant})$$

This quantity is key to the question of spontaneity under the conditions we usually work under. If for a process ΔG is positive it does not occur spontaneous and can only be made to occur if it is 'pumped', i.e. coupled with a process that has a negative ΔG. The latter is spontaneous.

> If $\Delta G = 0$ then the system is as ***equilibrium***.

6.1.1: Direction of the spontaneous change

Because the ΔS term contains the temperature T as coefficient the spontaneous direction of a process, e.g. a chemical reaction can **change** with temperature depending on the values of the enthalpy and the entropy change ΔH and ΔS. This is true for the melting process, e.g. for water below 0^oC we get water=>ice, above this temperature ice melts to water, but it also goes for chemical reactions.

✓ Example

Consider

$$\mathrm{NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)}$$

$\Delta_r H$ at 298K / 1 bar is -176.2 kJ. The change in entropy is -0.285 kJ/K so that at 298K ΔG is -91.21 kJ. Clearly this is a reaction that will proceed to the depletion of whatever is the limiting reagent on the left.

However at 618 K this is a different story. Above this temperature ΔG is positive! (assuming enthalpy and entropy have remained the same, which is almost but not completely true) The reaction will not proceed. Instead the *reverse* reaction would proceed spontaneously. The salt on the right would decompose in the two gases -base and acid- on the left.

6.1.2: Meaning of the ΔG term

As we have seen, ΔA can be related to the maximal amount of work that a system can perform at constant V and T. We can hold an analogous argument for ΔG except that V is not constant so that we have to consider volume work (zero at constant volume) .

$$dG = d(U + PV - TS) = dU - TdS - SdT - PdV + VdP$$

As $dU = TdS + \delta w_{rev}$

$$dG = \delta w_{rev} - SdT + VdP + PdV$$

As the later term is $-\delta w_{volume}$

$$dG = \delta w_{rev} - SdT + VdP - \delta w_{volume}$$

At constant T and P the two middle terms drop out

$$dG = \delta w_{rev} - \delta w_{volume} = \delta w_{otherusefulwork}$$

Note

ΔG stands for the (maximal) reversible, isobaric isothermal non-PV work that a certain spontaneous change can perform. The volume work may not be zero, but is corrected for.

6.1.3: Natural variables of G

Because $G \equiv H - TS$, we can write

$$\begin{aligned} dG &= dH - TdS - SdT \\ &= TdS + VdP - TdS - SdT = VdP - SdT \end{aligned}$$

The natural variables of G are pressure P and temperature T. This is what makes this function the most useful of the four U, H, A, and G: these are the natural variables of most of your laboratory experiments!

6.1.4: Summary

We now have developed the basic set of concepts and functions that together form the framework of thermodynamics. Let's summarize four very basic state functions:

state function	natural variables
$dU = -PdV + TdS$	$U(V,S)$
$dH = +VdP + TdS$	$H(P,S)$
$dA = -PdV - SdT$	$A(V,T)$
$dG = +VdP - SdT$	$G(P,T)$

Note:

1. The replacement of δq by TdS was based on *reversible* heat. This means that in the irreversible case the expressions for dU and dH become inequalities
2. We only include *volume* work in the above expressions. If other work (elastic, electrical e.g.) is involved extra terms need to be added: $dU = TdS - PdV + xdX$ etc.

We are now ready to begin applying thermodynamics to a number of very diverse situations, but we will first develop some useful partial differential machinery.

6.2: Thermodynamic Functions have Natural Variables

The fundamental thermodynamic equations follow from five primary thermodynamic definitions and describe internal energy, enthalpy, Helmholtz energy, and Gibbs energy in terms of their natural variables. Here they will be presented in their differential forms.

6.2.1: Introduction

The fundamental thermodynamic equations describe the thermodynamic quantities U, H, G, and A in terms of their natural variables. The term "natural variable" simply denotes a variable that is one of the convenient variables to describe U, H, G, or A. When considered as a whole, the four fundamental equations demonstrate how four important thermodynamic quantities depend on variables that can be controlled and measured experimentally. Thus, they are essentially equations of state, and using the fundamental equations, experimental data can be used to determine sought-after quantities like G or H.

6.2.2: First Law of Thermodynamics

The first law of thermodynamics is represented below in its differential form

$$dU = đq + đw$$

where

- U is the internal energy of the system,
- q is heat flow of the system, and
- w is the work of the system.

The "đ" symbol represent **inexact differentials** and indicates that both q and w are path functions. Recall that U is a state function. The first law states that internal energy changes occur only as a result of heat flow and work done.

It is assumed that w refers only to PV work, where

$$w = -\int p dV$$

The fundamental thermodynamic equation for internal energy follows directly from the first law and the principle of Clausius:

$$dU = đq + đw$$

$$dS = \frac{\delta q_{rev}}{T}$$

we have

$$dU = TdS + \delta w$$

Since only PV work is performed,

$$dU = TdS - pdV \tag{6.2.1}$$

The above equation is the fundamental equation for U with natural variables of entropy S and volume$V$.

6.2.2.1: Principle of Clausius

The *Principle of Clausius* states that the entropy change of a system is equal to the ratio of heat flow in a reversible process to the temperature at which the process occurs. Mathematically this is written as

$$dS = \frac{\delta q_{rev}}{T}$$

where

- S is the entropy of the system,
- q_{rev} is the heat flow of a reversible process, and
- T is the temperature in Kelvin.

6.2.3: Enthalpy

Mathematically, enthalpy is defined as

$$H = U + pV \tag{6.2.2}$$

where H is enthalpy of the system, p is pressure, and V is volume. The fundamental thermodynamic equation for enthalpy follows directly from it deffinition (Equation 6.2.2) and the fundamental equation for internal energy (Equation 6.2.1) :

$$dH = dU + d(pV)$$

$$= dU + pdV + VdP$$

$$dU = TdS - pdV$$

$$dH = TdS - pdV + pdV + Vdp$$

$$dH = TdS + Vdp$$

The above equation is the fundamental equation for H. The natural variables of enthalpy are S and p, entropy and pressure.

6.2.4: Gibbs Energy

The mathematical description of Gibbs energy is as follows

$$G = U + pV - TS = H - TS \tag{6.2.3}$$

where G is the Gibbs energy of the system. The fundamental thermodynamic equation for Gibbs Energy follows directly from its definition 6.2.3 and the fundamental equation for enthalpy 6.2.2:

$$dG = dH - d(TS)$$

$$= dH - TdS - SdT$$

Since

$$dH = TdS + VdP$$

$$dG = TdS + VdP - TdS - SdT$$

$$dG = VdP - SdT \tag{6.2.4}$$

The above equation is the fundamental equation for G. The natural variables of Gibbs energy are P and T.

6.2.5: Helmholtz Energy

Mathematically, Helmholtz energy is defined as

$$A = U - TS \tag{6.2.5}$$

where A is the Helmholtz energy of the system, which is often written as the symbol F. The fundamental thermodynamic equation for Helmholtz energy follows directly from its definition (Equation 6.2.5) and the fundamental equation for internal energy (Equation 6.2.1):

$$dA = dU - d(TS)$$

$$= dU - TdS - SdT$$

Since

$$dU = TdS - pdV$$

$$dA = TdS - pdV - TdS - SdT$$

$$dA = -pdV - SdT \tag{6.2.6}$$

Equation 6.2.6 is the fundamental equation for A with natural variables of V and T. For the definitions to hold, it is assumed that **only** PV work is done and that **only reversible** processes are used. These assumptions are required for the first law and the principle of Clausius to remain valid. Also, these equations do not account include n, the number of moles, as a variable. When n is included, the equations appear different, but the essence of their meaning is captured without including the n-dependence.

6.2.6: Chemical Potential

The fundamental equations derived above were not dependent on changes in the amounts of species in the system. Below the n-dependent forms are presented[1,4].

$$dU = TdS - PdV + \sum_{i=1}^{N} \mu_i dn_i$$

$$dH = TdS + VdP + \sum_{i=1}^{N} \mu_i dn_i$$

$$dG = -SdT + Vdp + \sum_{i=1}^{N} \mu_i dn_i$$

$$dA = -SdT - PdV + \sum_{i=1}^{N} \mu_i dn_i$$

where μ_i is the chemical potential of species i and dn_i is the change in number of moles of substance i.

6.2.7: Importance/Relevance of Fundamental Equations

The differential fundamental equations describe U, H, G, and A in terms of their natural variables. The natural variables become useful in understanding not only how thermodynamic quantities are related to each other, but also in analyzing relationships between measurable quantities (i.e. P, V, T) in order to learn about the thermodynamics of a system. Below is a table summarizing the natural variables for U, H, G, and A:

Thermodynamic Quantity	Natural Variables
U (internal energy)	S, V
H (enthalpy)	S, P
G (Gibbs energy)	T, P
A (Helmholtz energy)	T, V

6.2.8: Maxwell Relations

The fundamental thermodynamic equations are the means by which the Maxwell relations are derived[1,4]. The Maxwell Relations can, in turn, be used to group thermodynamic functions and relations into more general "families"[2,3].

As we said dA is an **exact differential**. Let's write is out in its natural variables (Equation 6.2.6) and take a cross derivative. The dA expression in natural variables is

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$

The partial derivatives of A of first order can already be quite interesting we see e.g. in step 2 that the first partial of A versus V (at T constant) is the negative of the pressure.

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

Likewise we find the (isochoric) slope with temperature gives us the negative of the entropy. Thus entropy is one of the ***first order derivatives*** of A.

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

When we apply a cross derivative

$$\left(\frac{\partial^2 A}{\partial V \partial T}\right) = \left(\frac{\partial(-S)}{\partial V}\right)_T + \left(\frac{\partial(-P)}{\partial T}\right)_V$$

we get what is known as a ***Maxwell relation***:

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

? Exercise

What does Equation three mean for the heat capacity? answer

A similar treatment of dG (Equation 6.2.4 gives:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

and another Maxwell relation

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

6.2.9: References

1. DOI: 10.1063/1.1749582
2. DOI: 10.1063/1.1749549
3. DOI:10.1103/PhysRev.3.273
4. *A Treatise on Physical Chemistry*, 3rd ed.; Taylor, H. S. and Glasstone, S., Eds.; D. Van Nostrand Company: New York, 1942; Vol. 1; p 454-485.

6.2.10: Problems

1. If the assumptions made in the derivations above were not made, what would effect would that have? Try to think of examples were these assumptions would be violated. Could the definitions, principles, and laws used to derive the fundamental equations still be used? Why or why not?
2. For what kind of system does the number of moles not change? This said, do the fundamental equations without n-dependence apply to a wide range of processes and systems?
3. Derive the Maxwell Relations.
4. Derive the expression

$$\left(\frac{\partial H}{\partial P}\right)_{T,n} = -T\left(\frac{\partial V}{\partial T}\right)_{P,n} + V$$

Then apply this equation to an ideal gas. Does the result seem reasonable?
5. Using the definition of Gibbs energy and the conditions observed at phase equilibria, derive the Clapeyron equation.

6.2.11: Answers

1. If it was not assumed that PV-work was the only work done, then the work term in the second law of thermodynamics equation would include other terms (e.g. for electrical work, mechanical work). If reversible processes were not assumed, the Principle of Clausius could not be used. One example of such situations could the movement of charged particles towards a region of like charge (electrical work) or an irreversible process like combustion of hydrocarbons or friction.
2. In general, a closed system of non-reacting components would fit this description. For example, the number of moles would not change for a closed system in which a gas is sealed (to prevent leaks) in a container and allowed to expand/is contracted.
3. See the Maxwell Relations section.

4. $(\frac{\partial H}{\partial P})_{T,n} = 0$ for an ideal gas. Since there are no interactions between ideal gas molecules, changing the pressure will not involve the formation or breaking of any intermolecular interactions or bonds.
5. See the third outside link.

Contributors and Attributions

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6.3: The Standard State for a Gas is an Ideal Gas at 1 Bar

Tabulated data are expressed in terms of a pure ideal gas (no mixing) at 1 bar, known as standard state conditions (SSC). Standard states are indicated with the $\circ$ symbol. These values are tabulated at a specific temperature, but that temperature can vary and is not included in the definition of SSC. No real gas has perfectly ideal behavior, but this definition of the standard state allows corrections for non-ideality to be made consistently for all the different gases.

6.4: The Gibbs-Helmholtz Equation

6.4.0.1: Ideal gas

For a mole of ideal gas we can use the gas law to integrate volume over pressure and we get

$$\Delta G_{molar} = RT\ln\left(\frac{P_2}{P_1}\right)$$

It is customary to identify one of the pressures (P$_1$} with the *standard state* of **1 bar** and use the plimsoll to indicate the fact that we are referring to a standard state by writing:

$$G_{molar}(P) = G^o{}_{molar} + RT\ln\left(\frac{P}{1}\right) = G^o{}_{molar} + RT\ln[P]$$

The fact that we are making the function intensive (per mole) is usually indicated by putting a bar over the G symbol, although this is often omitted for $G^{\ominus}{}_{molar}$

6.4.0.1: Solids

For solids the volume does not change very much with pressure (the *isothermal compressibility* κ is small), so can assume it more or less constant:

$$G(P_{final}) = G(P_{initial}) + \int V dP(\text{from init to final}) \approx G(P_{initial}) + V\int dP(\text{from init to final}) = G(P_{initial}) + V \Delta P$$

6.4.1: The Gibbs-Helmholtz Expression

$$\frac{G}{T} = \frac{H}{T} - S$$

Take the derivative under constant pressure of each side to get

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2} + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P$$

We make use of the relationship between C_p and H and C_p and S

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2} + \frac{C_P}{\cancel{T}} - \frac{C_P}{\cancel{T}} \tag{6.4.1}$$

$$= -\frac{H}{T^2} \tag{6.4.2}$$

We said before that S is a first order derivative of G. As you can see from this derivation the enthalpy H is also a first order derivative, albeit not of G itself, but of G/T.

$$\left(\frac{\partial \Delta G/T}{\partial T}\right)_P = -\frac{\triangle H}{T^2}$$

The last step in the derivation simply takes the step before twice -say for the G and H at the begin and end of a *process*- and subtracts the two identical equations leading to a Δ symbol. In this differential form the Gibbs-Helmholtz equation can be applied to any process.

6.4.2: Gibbs Energy as a Function of Temperature

If heat capacities are know from 0 K we could determine both enthalpy and entropy by integration:

$$S(T) = S(0) + \int_0^T \frac{C_p}{T} dT$$

$$H(T) = H(0) + \int_0^T C_p\ dT$$

As we have seen we must be careful at phase transitions such as melting or vaporization. At these points the curves are *discontinuous* and the derivative C_p is undefined.

$$H(T) = H(0) + \int_0^{T_{fus}} C_p(T)_{solid} dT + \Delta H_{fus} + \int_{T_{fus}}^{T_{boil}} C_p(T)_{liquid} dT + \Delta H_{vap} + etc. \tag{6.4.3}$$

$$\begin{aligned} S(T) &= S(0) + \int_0^{T_{fus}} \frac{C_p(T)_{solid}}{T} dT + \Delta S_{fus} + \int_{T_{fus}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T} dT + \Delta S_{vap} + etc. & (6.4.4) \\ &= S(0) + \int_0^{T_{fus}} \frac{C_p(T)_{solid}}{T} dT + \frac{\Delta H_{fus}}{T_{fus}} + \int_{T_{fus}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T} dT + \frac{\Delta H_{vap}}{T_{boil}} + etc. & (6.4.5) \end{aligned}$$

with $H(T=0) = \text{undefined}$ and $S(T=0) = 0$ from the third law of thermodynamics.

> We also discussed the fact that the third law allows us to define $S(0)$ as zero in most cases. For the enthalpy we cannot do that so that our curve is with respect to an undefined zero point. We really should plot $H(T) - H(0)$ and leave $H(0)$ undefined.

Because the Gibbs free energy $G = H - TS$ we can also construct a curve for G as a function of temperature, simply by combining the H and the S curves (Equations 6.4.3 and 6.4.5):

$$G(T) = H(T) - TS(T)$$

Interestingly, if we do so, the **discontinuities** at the phase transition points will **drop out** for G because at these points $\Delta_{trs} H = T_{trs} \Delta_{trs} S$. Therefore, G is **always** continuous.

The $H(0)$ problem does not disappear so that once again our curve is subject to an arbitrary offset in the y-direction. The best thing we can do is plot the quantity $G(T) - H(0)$ and leave the offset $H(0)$ undefined.

We have seen above that the derivative of G with temperature is $-S$. As entropy is always positive, this means that the G-curve is always *descending* with temperature. It also means that although the curve is *continuous* even at the phase transitions, the slope of the G curve is not, because the derivative $-S$ makes a jump there. Fig. 22.7 in the book shows an example of such a curve for benzene. Note the kinks in the curve at the mp and the boiling point.

6.E: Helmholtz and Gibbs Energies (Exercises)

In the mid 1920's the German physicist Werner Heisenberg showed that if we try to locate an electron within a region Δx; e.g. by scattering light from it, some momentum is transferred to the electron, and it is not possible to determine exactly how much momentum is transferred, even in principle. Heisenberg showed that consequently there is a relationship between the uncertainty in position Δx and the uncertainty in momentum Δp.

$$\Delta p \Delta x \geq \frac{\hbar}{2} \tag{6.E.1}$$

You can see from Equation 6.E.1 that as Δp approaches 0, Δx must approach ∞, which is the case of the free particle discussed previously.

This uncertainty principle, which also is discussed in Chapter 4, is a consequence of the wave property of matter. A wave has some finite extent in space and generally is not localized at a point. Consequently there usually is significant uncertainty in the position of a quantum particle in space. Activity 1 at the end of this chapter illustrates that a reduction in the spatial extent of a wavefunction to reduce the uncertainty in the position of a particle increases the uncertainty in the momentum of the particle. This illustration is based on the ideas described in the next section.

? Exercise $6.E.1$

Compare the minimum uncertainty in the positions of a baseball (mass = 140 gm) and an electron, each with a speed of 91.3 miles per hour, which is characteristic of a reasonable fastball, if the standard deviation in the measurement of the speed is 0.1 mile per hour. Also compare the wavelengths associated with these two particles. Identify the insights that you gain from these comparisons.

Index

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Sample Word 1 | Sample Definition 1

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