CHEM 4B TEXTBOOK



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UC Davis: Chem 4H
General Chemistry for Majors II

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UNIT I: CHEMICAL THERMODYNAMICS

Thermochemistry is the study of the energy and heat associated with chemical reactions and/or physical transformations. A reaction may release or absorb energy, and a phase change may do the same, such as in melting and boiling. Thermochemistry focuses on these energy changes, particularly on the system's energy exchange with its surroundings. Thermochemistry is useful in predicting reactant and product quantities throughout the course of a given reaction.

Chemical thermodynamics studies the nature of the role of entropy in the process of chemical reactions and provided the bulk of expansion and knowledge of the field. Other formulations of thermodynamics emerged in the following decades. The combination of enthalpy and entropy can be used to predict whether a reaction is spontaneous or non-spontaneous (i.e., favorable or unfavorable to occur). Statistical thermodynamics, or statistical mechanics, concerns itself with statistical predictions of the collective motion of particles from their microscopic behavior.

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I: FUNDAMENTALS OF THERMOCHEMISTRY (HEAT AND ENTHALPY)

This chapter introduces you to **thermochemistry**, a branch of chemistry that describes the energy changes that occur during chemical reactions. In some situations, the energy produced by chemical reactions is actually of greater interest to chemists than the material products of the reaction. For example, the controlled combustion of organic molecules, primarily sugars and fats, within our cells provides the energy for physical activity, thought, and other complex chemical transformations that occur in our bodies. Similarly, our energy-intensive society extracts energy from the combustion of fossil fuels, such as coal, petroleum, and natural gas, to manufacture clothing and furniture, heat your home in winter and cool it in summer, and power the car or bus that gets you to class and to the movies.

1.1: Systems, States and Processes

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Outside Links

- Barrow, Gordon M. "Thermodynamics should be built on energy-not on heat and work." J. Chem. Educ. **1988**: 65, 122.
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- King, Edward L. "Thermodynamics of the thermal decomposition of water by closed chemical cycles." *J. Chem. Educ.* **1981**, *58*, 975.
- Peckham, G. D., McNaught, Ian J. 'Heat and work are not "forms of energy".' J. Chem. Educ. **1993**: 70, 103.

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1.1: Systems, States and Processes

Learning Objectives

- To understand the concept of energy and its various forms.
- To know the relationship between energy, work, and heat.

Because energy takes many forms, only some of which can be seen or felt, it is defined by its effect on matter. For example, microwave ovens produce energy to cook food, but we cannot see that energy. In contrast, we can see the energy produced by a light bulb when we switch on a lamp. In this section, we describe the forms of energy and discuss the relationship between energy, heat, and work.

Forms of Energy

The forms of energy include thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy (Figure 1.1.1). Thermal energy results from atomic and molecular motion; the faster the motion, the greater the thermal energy. The temperature of an object is a measure of its thermal energy content. Radiant energy is the energy carried by light, microwaves, and radio waves. Objects left in bright sunshine or exposed to microwaves become warm because much of the radiant energy they absorb is converted to thermal energy. Electrical energy results from the flow of electrically charged particles. When the ground and a cloud develop a separation of charge, for example, the resulting flow of electrons from one to the other produces lightning, a natural form of electrical energy. Nuclear energy is stored in the nucleus of an atom, and chemical energy is stored within a chemical compound because of a particular arrangement of atoms.

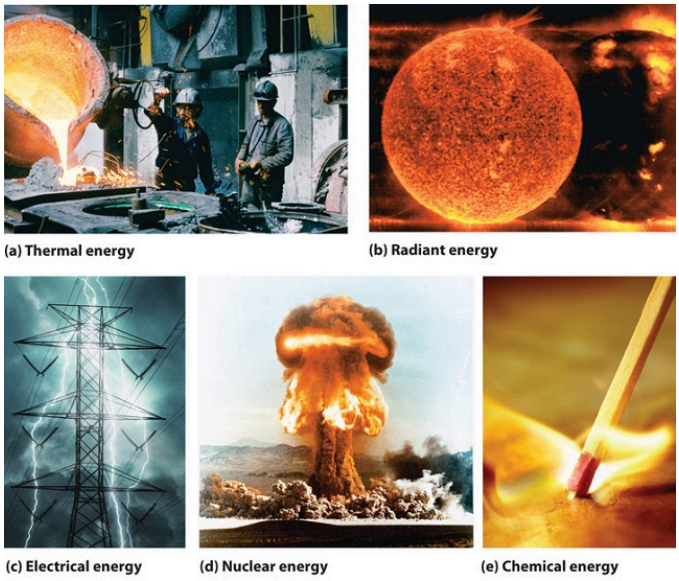


Figure 1.1.1: Forms of Energy. (a) *Thermal energy* results from atomic and molecular motion; molten steel at 2,000°C has high thermal energy. (b) *Radiant energy* (e.g., from the sun) is the energy in light, microwaves, and radio waves. (c) Lightning is an example of *electrical energy*, which is due to the flow of electrically charged particles. (d) *Nuclear energy* is released when particles in the nucleus of the atom are rearranged. (e) *Chemical energy* results from the particular arrangement of atoms in a chemical compound; the heat and light produced in this reaction are due to energy released during the breaking and reforming of chemical bonds. (CC BY-SA-NC 3.0; anonymous)

Electrical energy, nuclear energy, and chemical energy are different forms of potential energy (PE), which is energy stored in an object because of the relative positions or orientations of its components. A brick lying on the windowsill of a 10th-floor office has a great deal of potential energy, but until its position changes by falling, the energy is contained. In contrast, kinetic energy (KE) is energy due to the motion of an object. When the brick falls, its potential energy is transformed to kinetic energy, which is

then transferred to the object on the ground that it strikes. The electrostatic attraction between oppositely charged particles is a form of potential energy, which is converted to kinetic energy when the charged particles move toward each other.

Energy can be converted from one form to another (Figure 1.1.2) or, as we saw with the brick, transferred from one object to another. For example, when you climb a ladder to a high diving board, your body uses chemical energy produced by the combustion of organic molecules. As you climb, the chemical energy is converted to *mechanical work* to overcome the force of gravity. When you stand on the end of the diving board, your potential energy is greater than it was before you climbed the ladder: the greater the distance from the water, the greater the potential energy. When you then dive into the water, your potential energy is converted to kinetic energy as you fall, and when you hit the surface, some of that energy is transferred to the water, causing it to splash into the air. Chemical energy can also be converted to radiant energy; one common example is the light emitted by fireflies, which is produced from a chemical reaction.

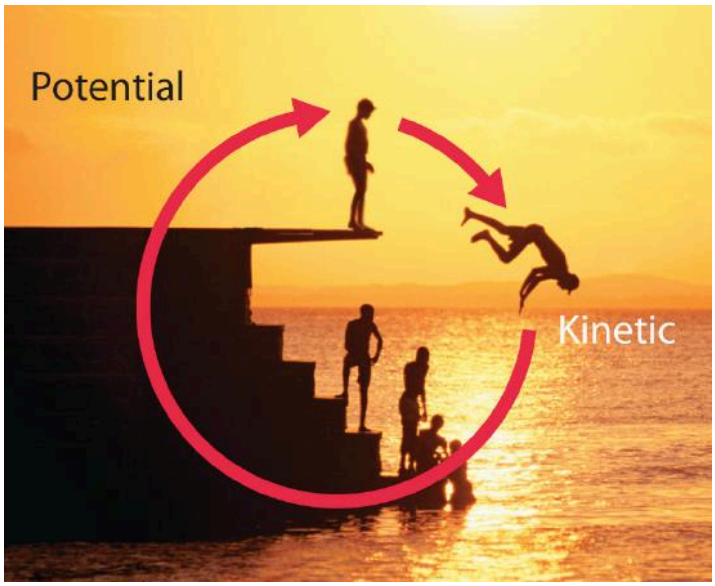


Figure 1.1.2: Interconversion of Forms of Energy. When a swimmer steps off the platform to dive into the water, potential energy is converted to kinetic energy. As the swimmer climbs back up to the top of the diving platform, chemical energy is converted to mechanical work. (CC BY-SA-NC 3.0; anonymous)

Although energy can be converted from one form to another, *the total amount of energy in the universe remains constant*. This is known as the **law of conservation of energy**: *Energy cannot be created or destroyed.*

Kinetic and Potential Energy

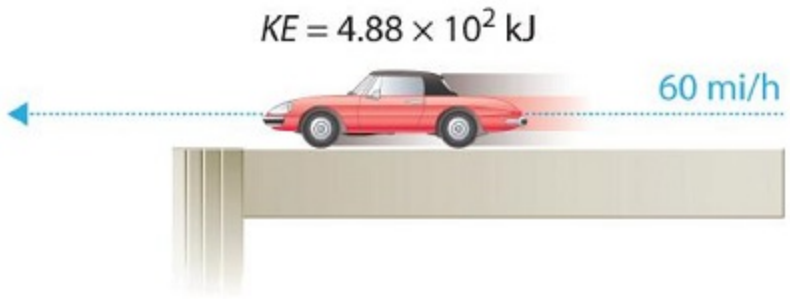
The kinetic energy of an object is related to its mass m and velocity v:

[redacted]

For example, the kinetic energy of a 1360 kg (approximately 3000 lb) automobile traveling at a velocity of 26.8 m/s (approximately 60 mi/h) is

[redacted]

Because all forms of energy can be interconverted, energy in any form can be expressed using the same units as kinetic energy. The SI unit of energy, the joule (J), is named after the British physicist James Joule (1818–1889), an early worker in the field of energy, is defined as 1 kilogram·meter^2/second^2 (kg·m^2/s^2). Because a joule is such a small quantity of energy, chemists usually express energy in kilojoules (1 kJ = 10^3 J). For example, the kinetic energy of the 1360 kg car traveling at 26.8 m/s is 4.88 × 10^5 J or 4.88 × 10^2 kJ. It is important to remember that *the units of energy are the same regardless of the form of energy*, whether thermal, radiant, chemical, or any other form. Because heat and work result in changes in energy, their units must also be the same.

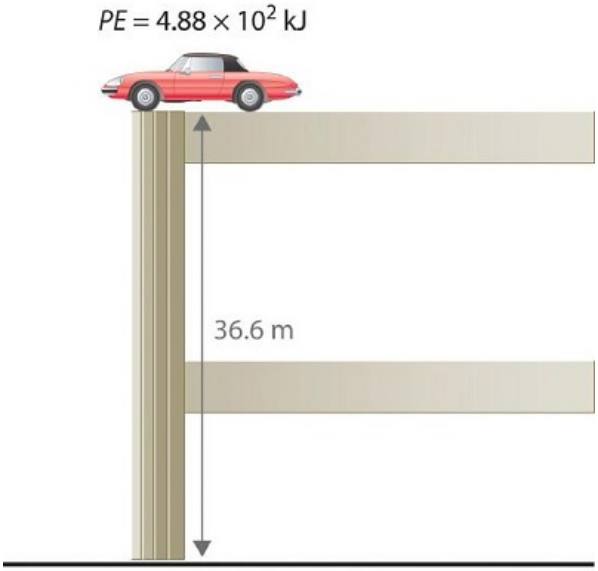


To demonstrate, let's calculate the potential energy of the same 1360 kg automobile if it were parked on the top level of a parking garage 36.6 m (120 ft) high. Its potential energy is equivalent to the amount of work required to raise the vehicle from street level to the top level of the parking garage, which is

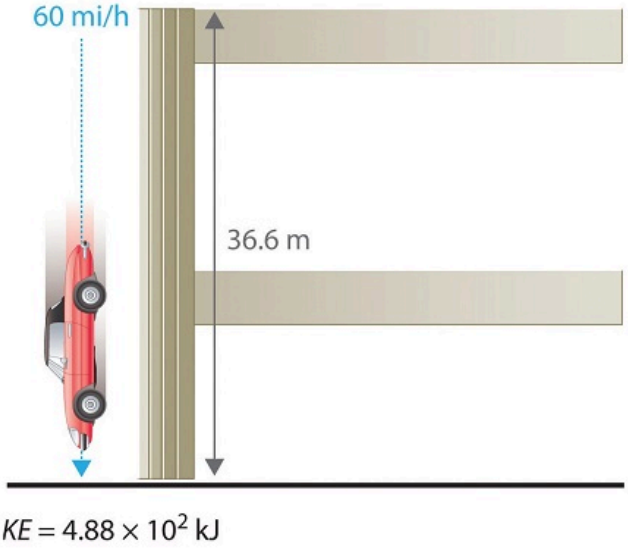
$$w = F\,d. \tag{1.1.1402}$$

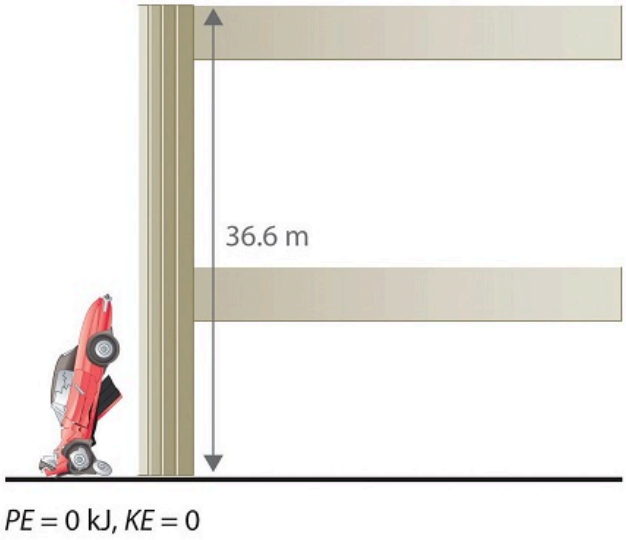
The force (F) exerted by gravity on any object is equal to its mass (m, in this case, 1360 kg) times the acceleration (a) due to gravity (*g*, 9.81 m/s^2 at Earth's surface). The distance (d) is the height (*h*) above street level (in this case, 36.6 m). Thus the potential energy of the car is as follows:

The units of potential energy are the same as the units of kinetic energy. Notice that in this case the potential energy of the stationary automobile at the top of a 36.6 m high parking garage is the same as its kinetic energy at 60 mi/h.



If the vehicle fell from the roof of the parking garage, its potential energy would be converted to kinetic energy, and it is reasonable to infer that the vehicle would be traveling at 60 mi/h just before it hit the ground, neglecting air resistance. After the car hit the ground, its potential and kinetic energy would both be zero.





Potential energy is usually defined relative to an arbitrary standard position (in this case, the street was assigned an elevation of zero). As a result, we usually calculate only differences in potential energy: in this case, the difference between the potential energy of the car on the top level of the parking garage and the potential energy of the same car on the street at the base of the garage.

Units of Energy

The units of energy are the same for all forms of energy. Energy can also be expressed in the non-SI units of calories (cal), where 1 cal was originally defined as the amount of energy needed to raise the temperature of exactly 1 g of water from 14.5 °C to 15.5 °C.We specify the exact temperatures because the amount of energy needed to raise the temperature of 1 g of water 1 °C varies slightly with elevation. To three significant figures, however, this amount is 1.00 cal over the temperature range 0 °C–100 °C. The name is derived from the Latin *calor*, meaning “heat.” Although energy may be expressed as either calories or joules, calories were defined in terms of heat, whereas joules were defined in terms of motion. Because calories and joules are both units of energy, however, the calorie is now defined in terms of the joule:

[redacted]

In this text, we will use the SI units—joules (J) and kilojoules (kJ)—exclusively, except when we deal with nutritional information.

Example 1.1.1: Kinetic Energy of Baseballs

a. If the mass of a baseball is 149 g, what is the kinetic energy of a fastball clocked at 100 mi/h?
b. A batter hits a pop fly, and the baseball (with a mass of 149 g) reaches an altitude of 250 ft. If we assume that the ball was 3 ft above home plate when hit by the batter, what is the increase in its potential energy?

Given

- mass and velocity or height

Asked for

- kinetic and potential energy

Strategy

Use Equation 1.1.849 to calculate the kinetic energy and Equation 1.1.852 to calculate the potential energy, as appropriate.

Solution

a. The kinetic energy of an object is given by $\frac{1}{2}mv^2$ In this case, we know both the mass and the velocity, but we must convert the velocity to SI units:

$$v = \left(\frac{100\ \cancel{mi}}{1\ \cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.61\ \cancel{km}}{1\ \cancel{mi}}\right)\left(\frac{1000\ m}{1\ \cancel{km}}\right)$$
$$= 44.7\ m/s$$

The kinetic energy of the baseball is therefore (via Equation 1.1.849)

$$KE = \frac{1}{2}149\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{44.7\ m}{s}\right)^2$$
$$= 1.49 \times 10^2\ \frac{kg \cdot m^2}{s^2}$$
$$= 1.49 \times 10^2\ J$$

b. The increase in potential energy is the same as the amount of work required to raise the ball to its new altitude, which is (250 – 3) = 247 feet above its initial position. Thus

$$PE = 149\ \cancel{g}\left(\frac{1\ kg}{1000\ \cancel{g}}\right)\left(\frac{9.81\ m}{s^2}\right)(247\ \cancel{ft})\left(\frac{0.3048\ m}{1\ \cancel{ft}}\right)$$
$$= 1.10 \times 10^2\ \frac{kg \cdot m^2}{s^2}$$
$$= 1.10 \times 10^2\ J$$

Exercise 1.1.1

a. In a bowling alley, the distance from the foul line to the head pin is $59\ ft$ and $10\ \frac{13}{16} in.$ (18.26 m). If a 16 lb (7.3 kg) bowling ball takes 2.0 s to reach the head pin, what is its kinetic energy at impact? (Assume its speed is constant.)
b. What is the potential energy of a 16 lb bowling ball held 3.0 ft above your foot?

Answer a

3.10×10^2 J

Answer b

65 J

Systems and Surroundings

To study the flow of energy during a chemical reaction, we need to distinguish between a system, the small, well-defined part of the universe in which we are interested (such as a chemical reaction), and its surroundings, the rest of the universe, including the container in which the reaction is carried out (Figure 1.1.3). In the discussion that follows, the mixture of chemical substances that undergoes a reaction is always the system, and the flow of heat can be from the system to the surroundings or vice versa.

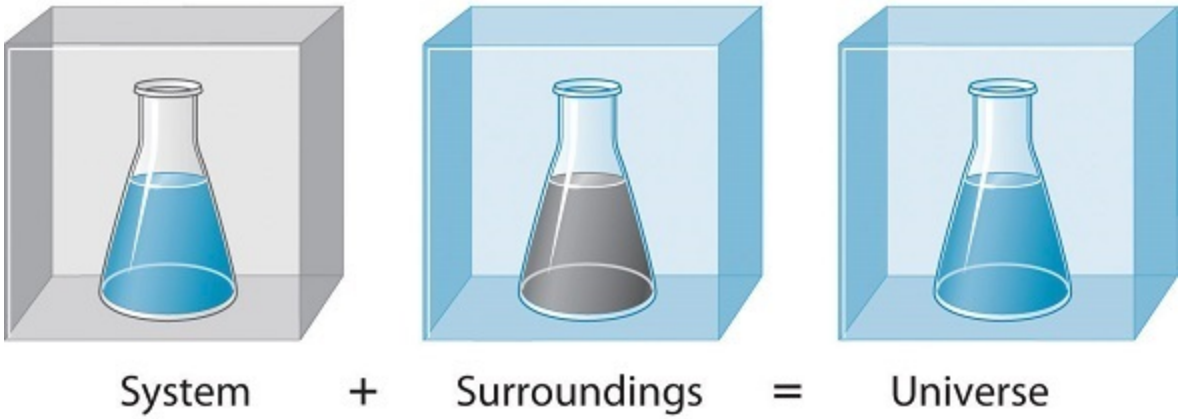


Figure 1.1.3: A System and Its Surroundings. The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out. (CC BY-SA-NC 3.0; anonymous)

Three kinds of systems are important in chemistry. An open system can exchange both matter and energy with its surroundings. A pot of boiling water is an open system because a burner supplies energy in the form of heat, and matter in the form of water vapor is lost as the water boils. A closed system can exchange energy but not matter with its surroundings. The sealed pouch of a ready-made dinner that is dropped into a pot of boiling water is a closed system because thermal energy is transferred to the system from the boiling water but no matter is exchanged (unless the pouch leaks, in which case it is no longer a closed system). An isolated system exchanges neither energy nor matter with the surroundings. Energy is always exchanged between a system and its surroundings, although this process may take place very slowly. A truly isolated system does not actually exist. An insulated thermos containing hot coffee approximates an isolated system, but eventually the coffee cools as heat is transferred to the surroundings. In all cases, the amount of heat lost by a system is equal to the amount of heat gained by its surroundings and vice versa. That is, *the total energy of a system plus its surroundings is constant*, which must be true if *energy is conserved*.

The state of a system is a complete description of a system at a given time, including its temperature and pressure, the amount of matter it contains, its chemical composition, and the physical state of the matter. A state function is a property of a system whose magnitude depends on only the present state of the system, not its previous history. Temperature, pressure, volume, and potential energy are all state functions. The temperature of an oven, for example, is independent of however many steps it may have taken for it to reach that temperature. Similarly, the pressure in a tire is independent of how often air is pumped into the tire for it to reach that pressure, as is the final volume of air in the tire. Heat and work, on the other hand, are not state functions because they are *path dependent*. For example, a car sitting on the top level of a parking garage has the same potential energy whether it was lifted by a crane, set there by a helicopter, driven up, or pushed up by a group of students (Figure 1.1.4). The amount of work expended to get it there, however, can differ greatly depending on the path chosen. If the students decided to carry the car to the top of the ramp, they would perform a great deal more work than if they simply pushed the car up the ramp (unless, of course, they neglected to release the parking brake, in which case the work expended would increase substantially!). The potential energy of the car is the same, however, no matter which path they choose.

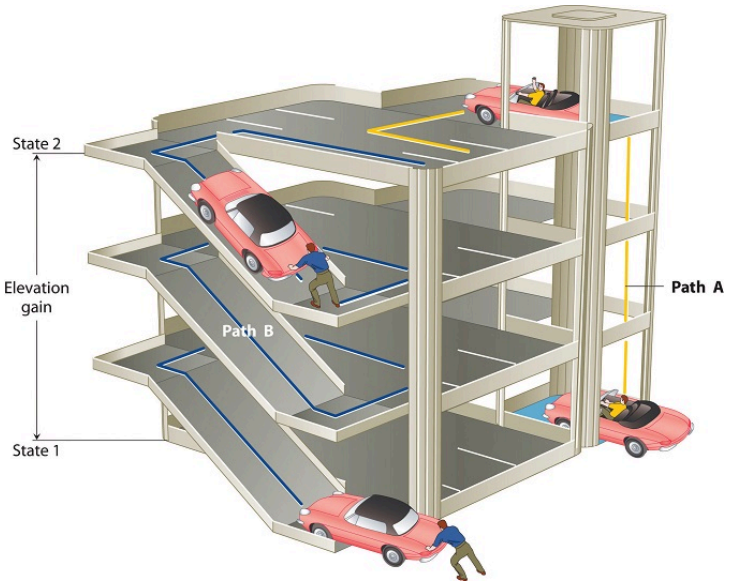


Figure 1.1.4: Elevation as an Example of a State Function. The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are *not* state functions. (CC BY-SA-NC 3.0; anonymous)

Summary

Thermochemistry is a branch of chemistry that qualitatively and quantitatively describes the energy changes that occur during chemical reactions. **Energy** is the capacity to do work. **Mechanical work** is the amount of energy required to move an object a given distance when opposed by a force. **Thermal energy** is due to the random motions of atoms, molecules, or ions in a substance. The **temperature** of an object is a measure of the amount of thermal energy it contains. **Heat (*q*)** is the transfer of thermal energy from a hotter object to a cooler one. Energy can take many forms; most are different varieties of **potential energy (*PE*)**, energy caused by the relative position or orientation of an object. **Kinetic energy (*KE*)** is the energy an object possesses due to its motion. Energy can be converted from one form to another, but the **law of conservation of energy** states that energy can be neither created nor destroyed. The most common units of energy are the **joule (J)**, defined as 1 $(kg \cdot m^2)/s^2$, and the **calorie**, defined as the amount of energy needed to raise the temperature of 1 g of water by 1°C (1 cal = 4.184 J).

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1.2: Heat as a Mechanism to Transfer Energy

Learning Objectives

- To calculate changes in internal energy
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

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 KE, and we say that the object is “cold” (Figure 1.2.1). 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.

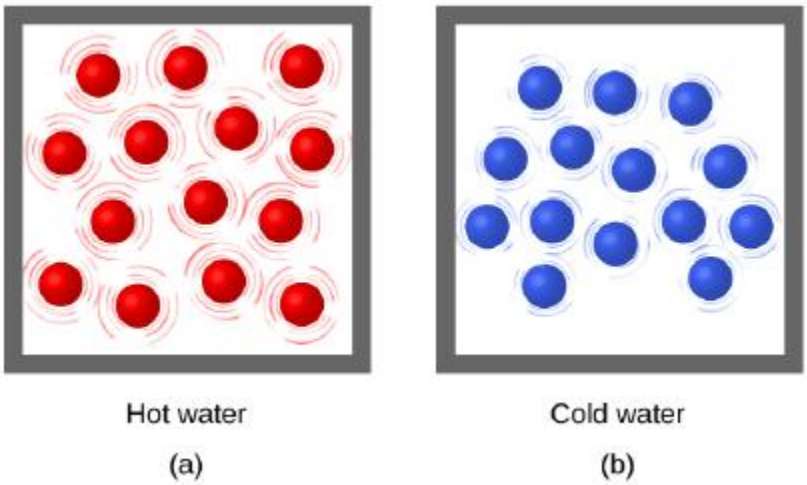


Figure 1.2.1: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

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 1.2.2).

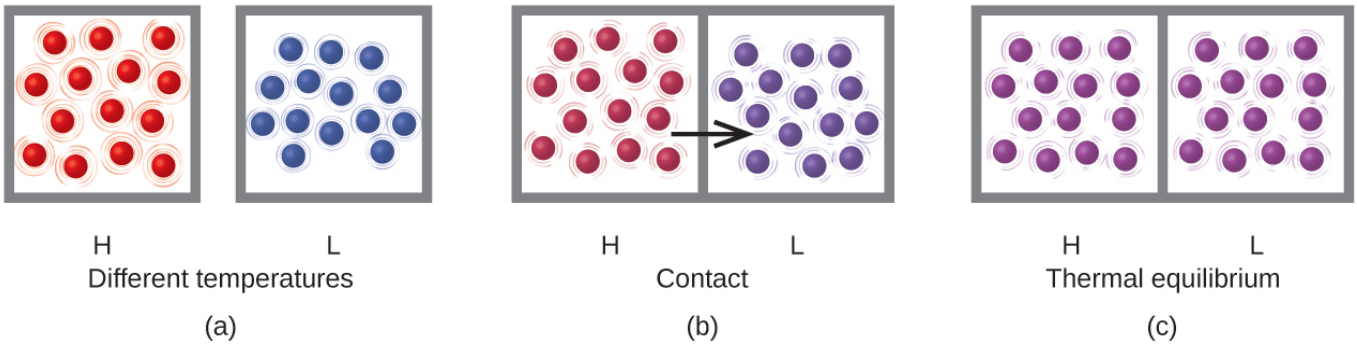


Figure 1.2.2: (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler 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.

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 1.2.3*a*). 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 1.2.3: (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).

Heat does not "Flow" nor does Heat "Transfer"

The definition of heat is the transfer of *thermal energy* between two bodies at different temperatures, since temperature is a measure of the average kinetic energy of a sample, this means that heat is the flow of kinetic energy from one spot to another. Therefore, heat is the process of the energy flow and a specific system; a system does not "contain" heat, therefore heat cannot be "transferred" nor does not "flow."

> The concept of heat flow originates from the incorrect theory in the 19th century called caloric theory that postulated that heat was connect to a mythical fluid that flows from hotter systems to colder systems. Unfortunately, the vernacular usage of terms involving heat flowing is ingrained in the English language and it is difficulty to avoid them in scientific discussions of thermodynamics. Nevertheless, it is important to emphasize that the important concept that heat does not flow.

Direction of Heat "Flow": Endothermic vs. Exothermic Processes

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel. The balanced chemical equation for the reaction is as follows:



We can also write this chemical equation as



to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (q) is transferred *from* a system *to* its surroundings is described as exothermic. By convention, $q < 0$ for an exothermic reaction.

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When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:



When heat is transferred *to* a system *from* its surroundings, the process is endothermic. By convention, $q > 0$ for an endothermic reaction. It is poor form to have a $heat$ term in the chemical reaction like in Equations $1.2.856$ and $1.2.857$ since heat is it not a

true species in the reaction. However, this is a convenient approach to represent exothermic and endothermic behavior and is commonly used by chemists.

By convention, $q < 0$ for an exothermic reaction and $q > 0$ for an endothermic reaction.

Exercise 1.2.1

Decide whether the following are endothermic or exothermic processes

a. water evaporates off a shower door
b. an acid tablet being added to a pool and the surrounding water heats up
c. $\mathrm{NH_4Cl}$ is dissolved in water and the solution cools
d. the burning of a log in a campfire

Hint

During an endothermic process heat is absorbed from surroundings, causing them to cool, so in every case where there is cooling there is most likely an endothermic process taking place. For exothermic reactions energy is being released to the surroundings and so the surroundings feel like they have been heated by the process.

Answer a

endothermic

Answer b

exothermic

Answer c

endothermic

Answer d

exothermic

Application: Heat can do more than increase temperature

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 1.2.4. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

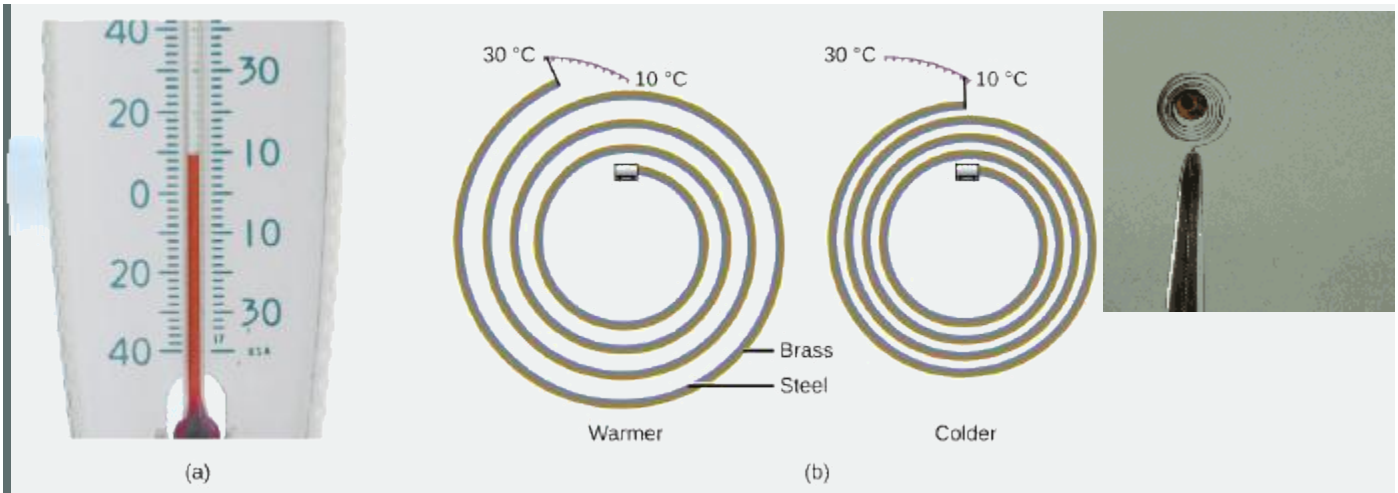


Figure 1.2.4: (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. 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). (c) The demonstration allows one to view the effects of heating and cooling a coiled bimetallic strip.A bimetallic coil from a thermometer reacts to the heat from a lighter, by uncoiling and then coiling back up when the lighter is removed. (CC BY-SA 4.0; hustvedt via Wikipedia)

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1.3: Work as a Mechanism to Transfer Energy

Learning Objectives

- To define work
- To identify mechanical and pressure-volume work

One definition of energy is the capacity to do work. There are many kinds of work, including mechanical work, electrical work, and work against a gravitational or a magnetic field. Here we will consider only mechanical work and focus on the work done during changes in the pressure or the volume of a gas.

Mechanical Work

The easiest form of work to visualize is mechanical work (Figure 1.3.1), which is the energy required to move an object a distance d when *opposed* by a force F, such as gravity (Figure 1.3.1):

[redacted]

with w is work, F is opposing force, and d is distance.

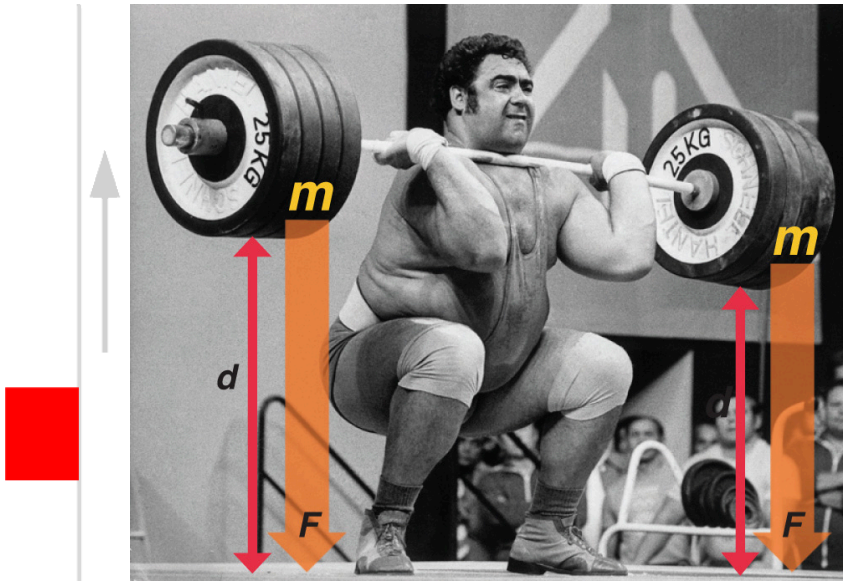


Figure 1.3.1: One form of energy is mechanical work, the energy required to move an object of mass m through distance d when opposed by a force F, i.e., as gravity. (CC BY-SA-NC; anonymous)

Because the force (F) that opposes the action is equal to the mass (m) of the object times its acceleration (a), Equation 1.3.858 can be rewritten to:

[redacted]

with w is work, m is mass, a is acceleration, and d is distance.

Recall from that weight is a force caused by the gravitational attraction between two masses, such as you and Earth. Hence for works against gravity (on Earth), a can be set to $g = 9.8\ m/s^2$. Consider the mechanical work required for you to travel from the first floor of a building to the second. Whether you take an elevator or an escalator, trudge upstairs, or leap up the stairs two at a time, energy is expended to overcome the opposing force of gravity. The amount of work done (*w*) and thus the energy required

depends on three things:

1. the height of the second floor (the distance d);
2. your mass, which must be raised that distance against the downward acceleration due to gravity; and
3. your path.

Pressure-Volume (PV) Work

To describe this pressure–volume work (PV work), we will use such imaginary oddities as frictionless pistons, which involve no component of resistance, and ideal gases, which have no attractive or repulsive interactions. Imagine, for example, an ideal gas, confined by a frictionless piston, with internal pressure P_{int} and initial volume V_i (Figure $1.3.2$). If $P_{ext} = P_{int}$, the system is at equilibrium; the piston does not move, and no work is done. If the external pressure on the piston (P_{ext}) is less than P_{int}, however, then the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings; that is, the final volume (V_f) will be greater than V_i. If $P_{ext} > P_{int}$, then the gas will be compressed, and the surroundings will perform work on the system.

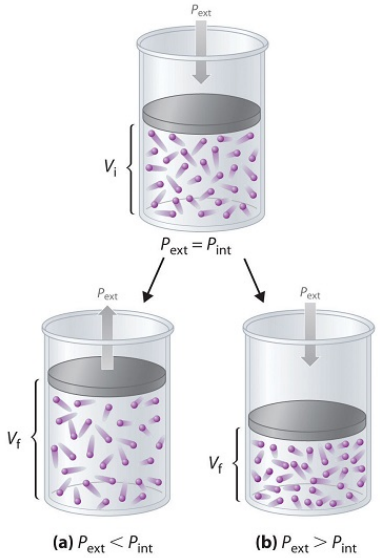


Figure $1.3.2$: PV Work demonstrated with a frictionless piston. (a) if the external pressure is less than P_{int}, the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings. The final volume (V_f) will be greater than V_i. (b) Alternatively, if the external pressure is greater than P_{int}, the gas will be compressed, and the surroundings will perform work on the system.

If the piston has cross-sectional area A, the external pressure exerted by the piston is, by definition, the force per unit area:

[redacted]

The volume of any three-dimensional object with parallel sides (such as a cylinder) is the cross-sectional area times the height ($V = Ah$). Rearranging Equation $10.8.845$ to give

$$F = P_{ext}A \tag{1.3.1403}$$

and defining the distance the piston moves (d) as Δh, we can calculate the magnitude of the work performed by the piston by substituting into Equation $1.3.858$:

[redacted]

The change in the volume of the cylinder (ΔV) as the piston moves a distance d is $\Delta V = A\Delta h$, as shown in Figure $1.3.3$.

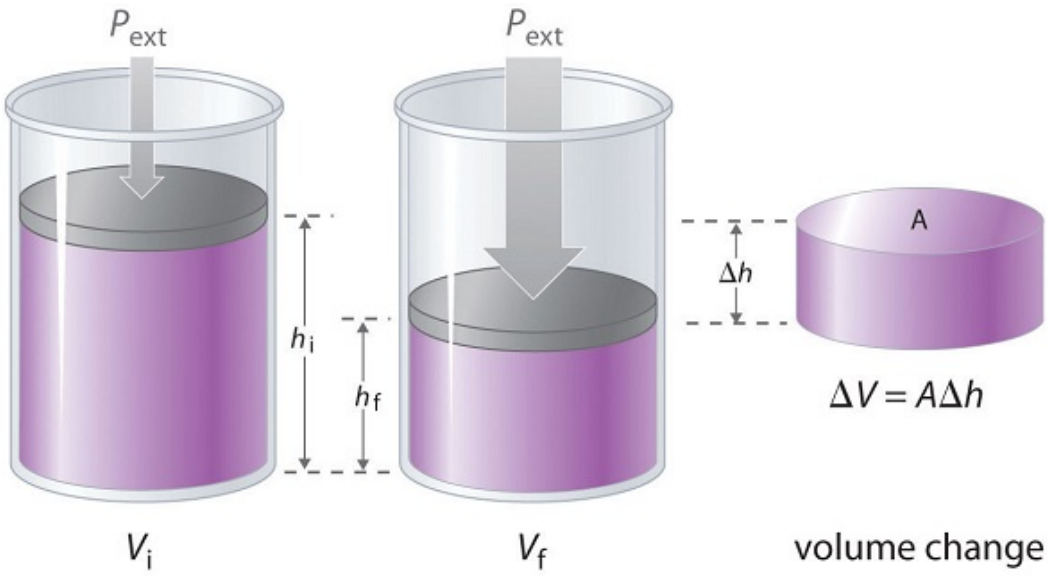


Figure 1.3.3: Work Performed with a change in volume. The change in the volume (ΔV) of the cylinder housing a piston is $\Delta V = A\Delta h$ as the piston moves. The work performed by the surroundings on the system as the piston moves inward is given by Equation 1.3.862.

The PV work performed is thus

[redacted]

The units of work obtained using this definition are correct for energy: pressure is force per unit area (newton/m^2) and volume has units of cubic meters, so

$$w = \left(\frac{F}{A}\right)_{\text{ext}} (\Delta V) = \frac{\text{newton}}{\text{m}^2} \times \text{m}^3 = \text{newton} \cdot \text{m} = \text{joule} \tag{1.3.1404}$$

If we use atmospheres for P and liters for V, we obtain units of L·atm for work. These units correspond to units of energy, as shown in the different values of the ideal gas constant R:

$$R = \frac{0.08206\ \text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = \frac{8.314\ \text{J}}{\text{mol} \cdot \text{K}} \tag{1.3.1405}$$

Thus 0.08206 L·atm = 8.314 J and 1 L·atm = 101.3 J.

Whether work is defined as having a positive sign or a negative sign is a matter of convention. Heat flow is defined from a system to its surroundings as negative; using that same sign convention, we define work done by a system on its surroundings as having a negative sign because it results in a transfer of energy from a system to its surroundings. This is an arbitrary convention and one that is not universally used. Some engineering disciplines are more interested in the work done on the surroundings than in the work done by the system and therefore use the opposite convention. Because $\Delta V > 0$ for an expansion, Equation 1.3.862 must be written with a negative sign to describe PV work done by the system as negative:

[redacted]

The work done by a gas expanding against an external pressure is therefore negative, corresponding to work done by a system on its surroundings. Conversely, when a gas is compressed by an external pressure, $\Delta V < 0$ and the work is positive because work is being done on a system by its surroundings.

A Matter of Convention

For the thermochemistry

- Heat is positive when energy is transferred from the surroundings to the system
- Work is positive when energy is transferred from the surroundings to the system

Example 1.3.2: Internal Combustion Engine

A small high-performance internal combustion engine has six cylinders with a total nominal displacement (volume) of 2.40 L and a 10:1 compression ratio (meaning that the volume of each cylinder decreases by a factor of 10 when the piston compresses the air–gas mixture inside the cylinder prior to ignition). How much work in joules is done when a gas in one cylinder of the engine expands at constant temperature against an opposing pressure of 40.0 atm during the engine cycle? Assume that the gas is ideal, the piston is frictionless, and no energy is lost as heat.

Given: final volume, compression ratio, and external pressure

Asked for: work done

Strategy

Calculate the final volume of gas in a single cylinder. Then compute the initial volume of gas in a single cylinder from the compression ratio. Use Equation 1.3.865 to calculate the work done in liter-atmospheres. Convert from liter-atmospheres to joules.

Solution

A To calculate the work done, we need to know the initial and final volumes. The final volume is the volume of one of the six cylinders with the piston all the way down: V_f = 2.40 L/6 = 0.400 L. With a 10:1 compression ratio, the volume of the same cylinder with the piston all the way up is V_i = 0.400 L/10 = 0.0400 L. Work is done by the system on its surroundings, so work is negative.

$$\begin{aligned} w &= -P_{ext}\Delta V \\ &= -(40.0\,atm)(0.400\,L - 0.0400\,L) \\ &= -14.4\,L \cdot atm \end{aligned}$$

Converting from liter-atmospheres to joules,

$$\begin{aligned} w &= -(14.4\ \text{L} \cdot \text{atm})[101.3\ \text{J}/(\text{L} \cdot \text{atm})] \\ &= -1.46 \times 10^3\ \text{J} \end{aligned}$$

In the following exercise, you will see that the concept of work is not confined to engines and pistons. It is found in other applications as well.

Exercise 1.3.2: Work required to Breath

Breathing requires work, even if you are unaware of it. The lung volume of a 70 kg man at rest changed from 2200 mL to 2700 mL when he inhaled, while his lungs maintained a pressure of approximately 1.0 atm.

a. How much work in liter-atmospheres and joules was required to take a single breath?
b. During exercise, his lung volume changed from 2200 mL to 5200 mL on each in-breath.
c. How much additional work in joules did he require to take a breath while exercising?

Answer

−0.500 L·atm, or −50.7 J; −304 J; if he takes a breath every three seconds, this corresponds to 1.4 Calories per minute (1.4 kcal).

Example 1.3.1: Expansion (PV) work

a. How much work is done by a gas that expands from 2 liters to 5 liters against an external pressure of 750 mmHg?
b. How much work is done by 0.54 moles of a gas that has an initial volume of 8 liters and expands under the following conditions: 30 °C and 1.3 atm?
c. How much work is done by a gas (P=1.7 atm, V=1.56 L) that expands against an external pressure of 1.8 atm?

Solution a

$$w = -P\Delta V$$

$$\Delta V = V_{final} - V_{Initial} = 5\,L - 2\,L = 3L$$

Convert 750 mmHg to atm:

$$750mmHg * 1/760(atm/mmHg) = 0.9868atm.$$

$$W = -p\Delta V = -(.9868\,atm)(3\,L) = -2.96\,L\,atm.$$

Solution b

First we must find the final volume using the ideal gas law:

$$pV = nRT$$

or

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

$$= \frac{(0.54\,moles)(0.082057(L\,atm)/(mol\,K))(303\,K)}{1.3\,atm} = 10.33\,L$$

$$\Delta V = V_{final} - V_{initial}$$

$$= 10.3\,L - 8\,L = 2.3\,L$$

Then from Equation 1.3.862

$$w = -p\Delta V = -(1.3\,atm)(2.3\,L) = -3\,L\cdot atm.$$

Solution c

$$w = -p\Delta V = -(1.8\,atm)\,\Delta V.$$

Given p_1, V_1, and p_2, find V_2: $p_1V_1 = p_2V_2$ (at constant T and n)

$$V_2 = \frac{V_1P_1}{P_2} = (1.56L * 1.7atm)/1.8atm = 1.47L$$

Now,

$$\Delta V = V_2 - V_1 = 1.47\,L - 1.56\,L = -0.09$$

$$w = -(1.8atm) * (-0.09L) = 0.162Latm.$$

Work in Chemical Transformations

Suppose, for example, that the system under study is a mass of steam heated by the combustion of several hundred pounds of coal and enclosed within a cylinder housing a piston attached to the crankshaft of a large steam engine. The gas is not ideal, and the cylinder is not frictionless. Nonetheless, as steam enters the engine chamber and the expanding gas pushes against the piston, the piston moves, so useful work is performed. In fact, PV work launched the Industrial Revolution of the 19th century and powers the internal combustion engine on which most of us still rely for transportation.

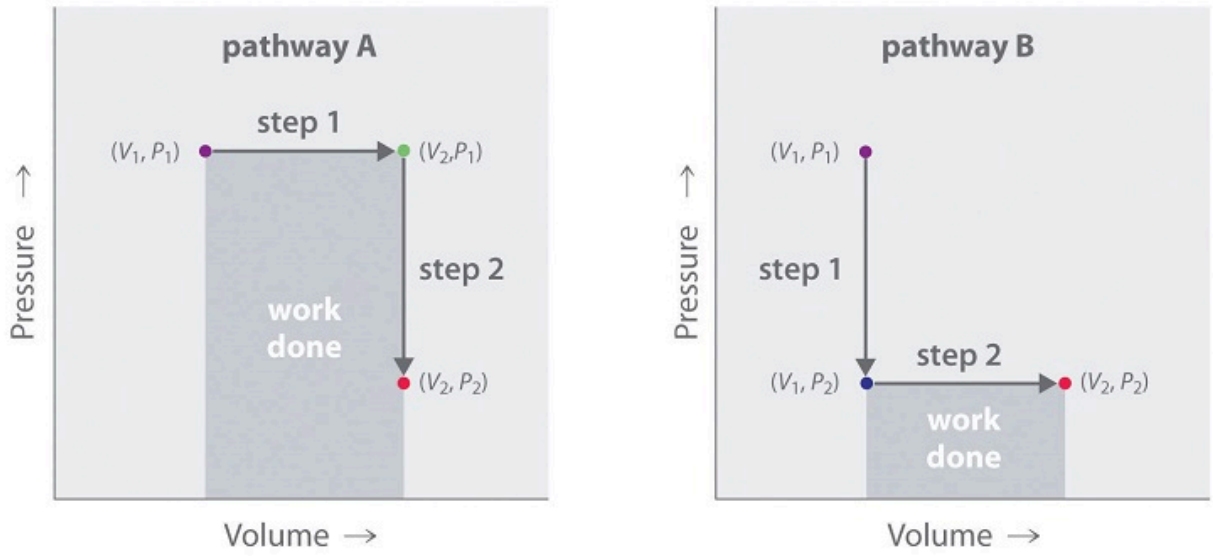


Figure 1.3.4: Work Is Not a State Function. In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1). Its pressure is then decreased while the volume remains constant (step 2). Pathway B reverses these steps. Although (V_1, P_1) and (V_2, P_2) are identical in both cases, the amount of work done (shaded area) depends on the pathway taken. (Cc BY-NC-SA; Anonymous by request)

In contrast to internal energy, work is not a state function. We can see this by examining Figure 1.3.4, in which two different, two-step pathways take a gaseous system from an initial state to a final state with corresponding changes in temperature. In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1); then its pressure is decreased while the volume remains constant (step 2). In pathway B, the order of the steps is reversed. The temperatures, pressures, and volumes of the initial and final states are identical in both cases, but the amount of work done, indicated by the shaded areas in the figure, is substantially different. As we can see, the amount of work done depends on the pathway taken from (V_1, P_1) to (V_2, P_2), which means that work is **not** a state function.

Internal energy is a state function, whereas work is not.

Work and Chemical Reactions

Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:



If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (Figure 1.3.5). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of *PV* work done by multiplying the external pressure *P* by the change in volume caused by movement of the piston (ΔV). At a constant external pressure (here, atmospheric pressure)

The negative sign associated with PV work done indicates that the system loses energy. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

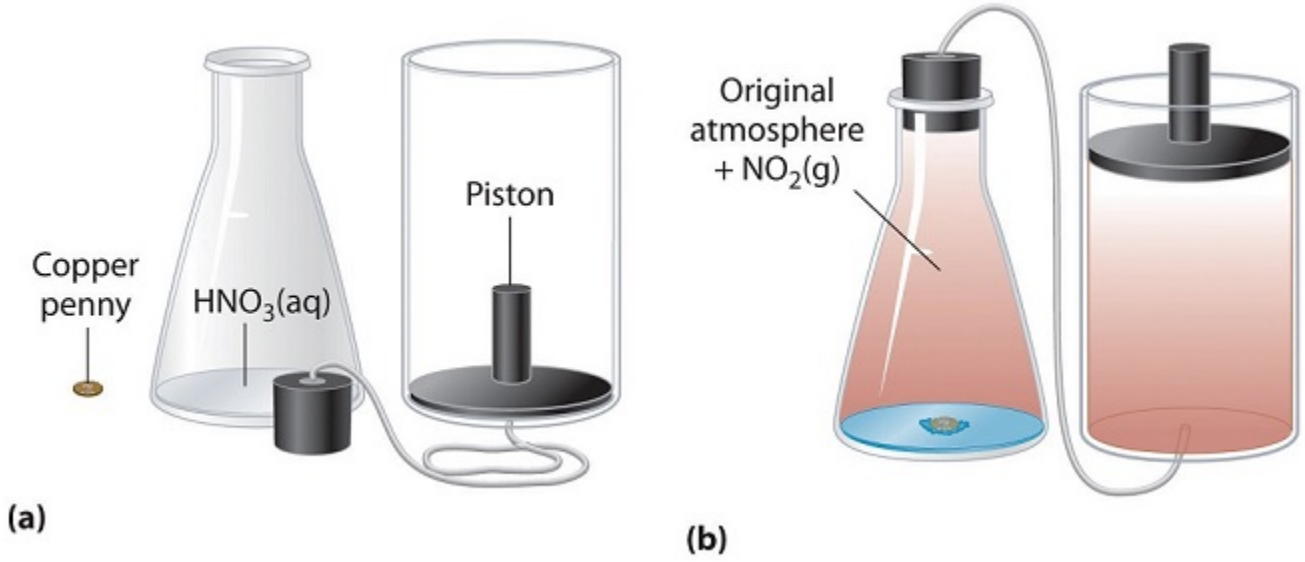


Figure 1.3.5: An Example of Work Performed by a Reaction Carried Out at Constant Pressure. (a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings.

Enthalpy

The symbol U represents the internal energy of a system, which is the sum of the kinetic energy and potential energy of all its components. It is the change in internal energy that produces heat plus work. To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called enthalpy (H) (from the Greek *enthalpein*, meaning "to warm"). The enthalpy of a system is defined as the sum of its internal energy U plus the product of its pressure P and volume V:

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function.

If a chemical change occurs at constant pressure (i.e., for a fixed P, $\Delta P = 0$), the change in enthalpy (ΔH) is

Substituting $q + w$ for ΔU (Equation 1.3.871) and $-w$ for $P\Delta V$ (Equation 1.3.867), we obtain

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 1.3.872 we see that at constant pressure the change in enthalpy, ΔH of the system, defined as $H_{final} - H_{initial}$, is equal to the heat gained or lost.

Just as with ΔU, because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. Most important, the enthalpy change is the same even if the process does *not* occur at constant pressure.

To find ΔH for a reaction, measure q_p under constant pressure.

Summary

All forms of energy can be interconverted. Three things can change the energy of an object: the transfer of heat, work performed on or by an object, or some combination of heat and work.

Outside Links

- Gasparro, Frances P. "Remembering the sign conventions for q and w in deltaU = q - w." J. Chem. Educ. 1976: 53, 389.
- Koubek, E. "PV work demonstration (TD)." J. Chem. Educ. 1980: 57, 374. '

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1.4: The First Law of Thermodynamics

Learning Objectives

- To calculate changes in internal energy
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

The relationship between the energy change of a system and that of its surroundings is given by the first law of thermodynamics, which states that the energy of the universe is constant. We can express this law mathematically as follows:

[redacted]

or

[redacted]

where the subscripts *univ*, *sys*, and *surr* refer to the universe, the system, and the surroundings, respectively. Thus the change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

> The tendency of all systems, chemical or otherwise, is to move toward the state with the lowest possible energy.

An important factor that determines the outcome of a chemical reaction is the tendency of all systems, chemical or otherwise, to move toward the lowest possible overall energy state. As a brick dropped from a rooftop falls, its potential energy is converted to kinetic energy; when it reaches ground level, it has achieved a state of lower potential energy. Anyone nearby will notice that energy is transferred to the surroundings as the noise of the impact reverberates and the dust rises when the brick hits the ground. Similarly, if a spark ignites a mixture of isooctane and oxygen in an internal combustion engine, carbon dioxide and water form spontaneously, while potential energy (in the form of the relative positions of atoms in the molecules) is released to the surroundings as heat and work. The internal energy content of the $\mathrm{CO_2/H_2O}$ product mixture is less than that of the isooctane $\mathrm{O_2}$ reactant mixture. The two cases differ, however, in the form in which the energy is released to the surroundings. In the case of the falling brick, the energy is transferred as work done on whatever happens to be in the path of the brick; in the case of burning isooctane, the energy can be released as solely heat (if the reaction is carried out in an open container) or as a mixture of heat and work (if the reaction is carried out in the cylinder of an internal combustion engine). Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred (q) and the work done (w):

[redacted]

Although q and w are not state functions on their own, their sum (ΔU_{sys}) is independent of the path taken and is therefore a state function. A major task for the designers of any machine that converts energy to work is to maximize the amount of work obtained and minimize the amount of energy released to the environment as heat. An example is the combustion of coal to produce electricity. Although the maximum amount of energy available from the process is fixed by the energy content of the reactants and the products, the fraction of that energy that can be used to perform useful work is not fixed. Because we focus almost exclusively on the changes in the energy of a system, we will not use “sys” as a subscript unless we need to distinguish explicitly between a system and its surroundings.

> Although q and w are not state functions, their sum (ΔU_{sys}) is independent of the path taken and therefore is a difference of a state function.

Example 1.4.1

A sample of an ideal gas in the cylinder of an engine is compressed from 400 mL to 50.0 mL during the compression stroke against a constant pressure of 8.00 atm. At the same time, 140 J of energy is transferred from the gas to the surroundings as heat. What is the total change in the internal energy (ΔU) of the gas in joules?

Given: initial volume, final volume, external pressure, and quantity of energy transferred as heat

Asked for: total change in internal energy

Strategy:

A. Determine the sign of q to use in Equation 1.4.876.
B. From Equation 1.4.876 calculate w from the values given. Substitute this value into Equation 1.4.876 to calculate ΔU.

Solution

A From Equation 1.4.876, we know that $\Delta U = q + w$ (First Law of Thermodynamics). We are given the magnitude of q (140 J) and need only determine its sign. Because energy is transferred from the system (the gas) to the surroundings, q is negative by convention.

B Because the gas is being compressed, we know that work is being done on the system, so w must be positive. From Equation 1.4.876,

$$\begin{aligned} w &= -P_{\text{ext}}\Delta V \\ &= -8.00\ \text{atm}(0.0500\ \text{L} - 0.400\ \text{L})\left(\frac{101.3\ \text{J}}{\text{L}\cdot\text{atm}}\right) \\ &= 284\ \text{J} \end{aligned}$$

Thus

$$\begin{aligned} \Delta U &= q + w \\ &= -140\ J + 284\ J \\ &= 144\ J \end{aligned}$$

In this case, although work is done on the gas, increasing its internal energy, heat flows from the system to the surroundings, decreasing its internal energy by 144 J. The work done and the heat transferred can have opposite signs.

Exercise 1.4.1

A sample of an ideal gas is allowed to expand from an initial volume of 0.200 L to a final volume of 3.50 L against a constant external pressure of 0.995 atm. At the same time, 117 J of heat is transferred from the surroundings to the gas. What is the total change in the internal energy (ΔU) of the gas in joules?

Answer

–216 J

By convention, both heat flow and work have a negative sign when energy is transferred from a system to its surroundings and vice versa.

Summary

The first law of thermodynamics states that the energy of the universe is constant. The change in the internal energy of a system is the sum of the heat transferred and the work done. The heat flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for ΔU.

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1.5: Heat Capacity and Calorimetry

Learning Objectives

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data
- To use calorimetric data to calculate enthalpy changes.

Heat Capacity

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

[redacted]

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

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,140 J of energy to raise the temperature of the pan by 50.0 °C

[redacted]

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:

[redacted]

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):

[redacted]

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:

[redacted]

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:

[redacted]

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 1.5.1).



Figure 1.5.1: Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (CC BY 4.0; Mark Blaser via OpenStax).

The heat capacity of an object depends on both its *mass* and its *composition*. For example, doubling the mass of an object doubles its heat capacity. Consequently, the amount of substance must be indicated when the heat capacity of the substance is reported. The molar heat capacity (C_p) is the amount of energy needed to increase the temperature of 1 mol of a substance by 1°C; the units of C_p are thus J/(mol•°C).The subscript *p* indicates that the value was measured at constant pressure. The specific heat (c_s) is the amount of energy needed to increase the temperature of 1 g of a substance by 1°C; its units are thus J/(g•°C).

We can relate the quantity of a substance, the amount of heat transferred, its heat capacity, and the temperature change either via moles (Equation 1.3.868) or mass (Equation 1.3.871):

[redacted]

where

- n is the number of moles of substance and
- c_p is the *molar heat capacity* (i.e., heat capacity per **mole** of substance), and
- $\Delta T = T_{final} - T_{initial}$ is the temperature change.

[redacted]

where

- m is the mass of substance in grams,
- c_s is the *specific heat* (i.e., heat capacity per **gram** of substance), and
- $\Delta T = T_{final} - T_{initial}$ is the temperature change.

Both Equations 1.3.868 and 1.3.871 are under constant pressure (which matters) and both show that we know the amount of a substance and its specific heat (for mass) or molar heat capcity (for moles), we can determine the amount of heat, q, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost.

The specific heats of some common substances are given in Table 1.5.1. Note that the specific heat values of most solids are less than 1 J/(g•°C), whereas those of most liquids are about 2 J/(g•°C). Water in its solid and liquid states is an exception. The heat capacity of ice is twice as high as that of most solids; the heat capacity of liquid water, 4.184 J/(g•°C), is one of the highest known. The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table 1.5.1.

Table 1.5.1: 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	mixture	1.007
oxygen	$O_2(g)$	0.918
aluminum	Al(s)	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	Ar(*g*)	0.522
iron	Fe(s)	0.449
copper	Cu(s)	0.385
lead	Pb(s)	0.130
gold	Au(s)	0.129
silicon	Si(s)	0.712
quartz	$SiO_2(s)$	0.730

The value of C is intrinsically a positive number, but ΔT and q can be either positive or negative, and they both must have the same sign. If ΔT and q are positive, then *heat flows from the surroundings into an object*. If ΔT and q are negative, then *heat flows from an object into its surroundings*.

If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, then $\Delta T > 0$ and q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, so $\Delta T < 0$ and q is negative.

Example 1.5.1: 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, 800 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C (Table 1.5.1), so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need 800 times as much to heat 800 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need 64 times as much to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using Equation 1.3.871:

$$\begin{aligned} q &= mc_s\Delta T \\ &= mc_s(T_{\text{final}} - T_{\text{initial}}) \\ &= (4.184\ \text{J/}\cancel{\text{g}}^\circ\text{C}) \times (800\ \cancel{\text{g}}) \times (85 - 21)^\circ\text{C} \\ &= (4.184\ \text{J/}\cancel{\text{g}}^\circ\cancel{\text{C}}) \times (800\ \cancel{\text{g}}) \times (64)^\circ\cancel{\text{C}} \\ &= 210,000\ \text{J} (= 210\ \text{kJ}) \end{aligned}$$

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

Exercise 1.5.1

How much heat, in joules, must be added to a 5.00×10^2 g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.451 J/g °C.

Answer

5.07×10^4 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 1.5.2: Determining Other Quantities

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

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using Equation 1.3.871:

$$q = mc_s\Delta T \qquad = mc_s(T_{final} - T_{initial})$$

Substituting the known values:

$$6,640\ J = (348\ g)c_s(43.6 - 22.4)\ ^\circ C$$

Solving:

$$c = \frac{6,640\ J}{(348\ g)(21.2^\circ C)} = 0.900\ J/g\ ^\circ C$$

Comparing this value with the values in Table 1.5.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

Exercise 1.5.2

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

Answer

$c = 0.45\ \ J/g\ \ ^\circ C$; the metal is likely to be iron from checking Table 1.5.1.

Example 1.5.3: Solar Heating

A home solar energy storage unit uses 400 L of water for storing thermal energy. On a sunny day, the initial temperature of the water is 22.0°C. During the course of the day, the temperature of the water rises to 38.0°C as it circulates through the water wall. How much energy has been stored in the water? (The density of water at 22.0°C is 0.998 g/mL.)



Passive solar system. During the day (a), sunlight is absorbed by water circulating in the water wall. At night (b), heat stored in the water wall continues to warm the air inside the house.

Given: volume and density of water and initial and final temperatures

Asked for: amount of energy stored

Strategy:

A. Use the density of water at 22.0°C to obtain the mass of water (m) that corresponds to 400 L of water. Then compute ΔT for the water.
B. Determine the amount of heat absorbed by substituting values for m, c_s, and ΔT into Equation 1.3.858.

Solution A

The mass of water is

$$mass\ of\ H_2O = 400\ \cancel{L}\left(\frac{1000\ \cancel{mL}}{1\ \cancel{L}}\right)\left(\frac{0.998\ g}{1\ \cancel{mL}}\right) = 3.99 \times 10^5 g\ H_2O$$

The temperature change (ΔT) is 38.0°C – 22.0°C = +16.0°C.

Solution B

From Table 1.5.1, the specific heat of water is 4.184 J/(g•°C). From Equation 1.3.871, the heat absorbed by the water is thus

$$q = mc_s\Delta T = \left(3.99 \times 10^5 \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^\circ C}}\right)\left(16.0\ \cancel{^\circ C}\right) = 2.67 \times 10^7 J = 2.67 \times 10^4 kJ$$

Both q and \9ΔT\) are positive, consistent with the fact that the water has absorbed energy.

Exercise 1.5.3: Solar Heating

Some solar energy devices used in homes circulate air over a bed of rocks that absorb thermal energy from the sun. If a house uses a solar heating system that contains 25000 kg of sandstone rocks, what amount of energy is stored if the temperature of the rocks increases from 20.0°C to 34.5°C during the day? Assume that the specific heat of sandstone is the same as that of quartz (SiO_2) in Table 1.5.1.

Answer

$2.7 \times 10^4\ kJ$

Even though the mass of sandstone is more than six times the mass of the water in Example 1.5.1, the amount of thermal energy stored is the same to two significant figures.

Heat "Flow" to Thermal Equilibrium

When two objects at different temperatures are placed in contact, heat flows from the warmer object to the cooler one until the temperature of both objects is the same. The law of conservation of energy says that the total energy cannot change during this process:

[redacted]

The equation implies that the amount of heat that flows *from* a warmer object is the same as the amount of heat that flows *into* a cooler object. Because the direction of heat flow is opposite for the two objects, the sign of the heat flow values must be opposite:

[redacted]

Thus heat is conserved in any such process, consistent with the law of conservation of energy.

> The amount of heat lost by a warmer object equals the amount of heat gained by a cooler object.

Substituting for q from Equation 1.3.871 gives

[redacted]

which can be rearranged to give

[redacted]

When two objects initially at different temperatures are placed in contact, we can use Equation 1.5.877 to calculate the final temperature if we know the chemical composition and mass of the objects.

Example 1.5.4: Thermal Equilibration of Copper and Water

If a 30.0 g piece of copper pipe at 80.0°C is placed in 100.0 g of water at 27.0°C, what is the final temperature? Assume that no heat is transferred to the surroundings.

Given: mass and initial temperature of two objects

Asked for: final temperature

Strategy: Using Equation 1.5.877 and writing $\Delta T = T_{final} - T_{initial}$ for both the copper and the water, substitute the appropriate values of m, c_s, and $T_{initial}$ into the equation and solve for T_{final}.

Solution

We can adapt Equation 1.5.877 to solve this problem, remembering that \(ΔT= T_{final} – T_{initial}\):

$$[mc_s\,(T_{final} - T_{initial})]_{Cu} + [mc_s\,(T_{final} - T_{initial})]_{H_2O} = 0$$

Substituting the data provided in the problem and Table 1.5.1 gives

$$\begin{aligned}(30\ g)\,(0.385\ J/(g°C))(T_{final} - 80°C) + (100\ g)(4.184\ J/(g°C))(T_{final} - 27.0°C) &= 0\\ T_{final}\,(11.6\ J/^oC) - 924\ J + T_{final}\,(418.4\ J/^oC) - 11,300\ J &= 0\\ T_{final}\,(430\ J/\,(g\cdot{}^o\,C)) &= 12,224\ J\\ T_{final} &= 28.4\ ^oC\end{aligned}$$

Exercise 1.5.4A: Thermal Equilibration of Gold and Water

If a 14.0 g chunk of gold at 20.0°C is dropped into 25.0 g of water at 80.0°C, what is the final temperature if no heat is transferred to the surroundings?

Answer

80.0°C

Exercise 1.5.4B: Thermal Equilibration of Aluminum and Water

A 28.0 g chunk of aluminum is dropped into 100.0 g of water with an initial temperature of 20.0°C. If the final temperature of the water is 24.0°C, what was the initial temperature of the aluminum? (Assume that no heat is transferred to the surroundings.)

Answer

90.6°C

Measuring Heat "Flow"

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The change in temperature of the measuring part of the calorimeter is converted into the amount of heat (since the previous calibration was used to establish its heat capacity). The measurement of heat transfer using this

approach requires the definition of a system (the substance or substances undergoing the chemical or physical change) and its surroundings (the other components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system). Knowledge of the heat capacity of the surroundings, and careful measurements of the masses of the system and surroundings and their temperatures before and after the process allows one to calculate the heat transferred as described in this section.

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process.

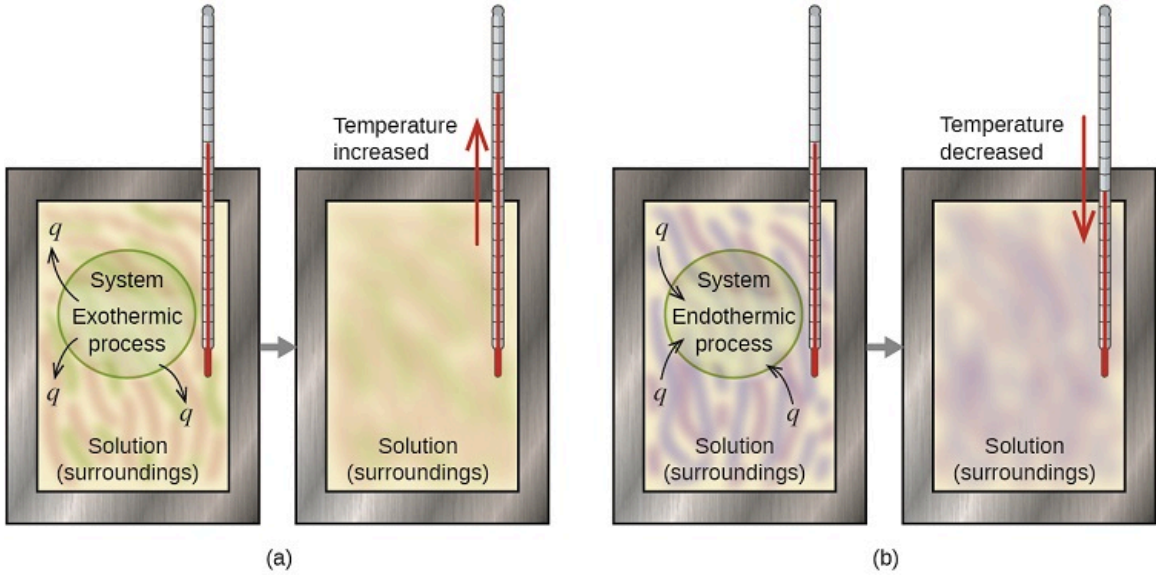


Figure 1.5.2: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system.

The thermal energy change accompanying a chemical reaction is responsible for the change in temperature that takes place in a calorimeter. If the reaction releases heat ($q_{rxn} < 0$), then heat is absorbed by the calorimeter ($q_{calorimeter} > 0$) and its temperature increases. Conversely, if the reaction absorbs heat ($q_{rxn} > 0$), then heat is transferred from the calorimeter to the system ($q_{calorimeter} < 0$) and the temperature of the calorimeter decreases. In both cases, *the amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction*. The heat capacity of the calorimeter or of the reaction mixture may be used to calculate the amount of heat released or absorbed by the chemical reaction. The amount of heat released or absorbed per gram or mole of reactant can then be calculated from the mass of the reactants.

> *The amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction.*

Constant-Pressure Calorimetry

Because ΔH is defined as the heat flow at constant pressure, measurements made using a constant-pressure calorimeter (a device used to measure enthalpy changes in chemical processes at constant pressure) give ΔH values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. A “student” version, called a *coffee-cup calorimeter* (Figure 1.5.3), is often encountered in general chemistry laboratories. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as several millionths of a degree (10^{-6} °C).

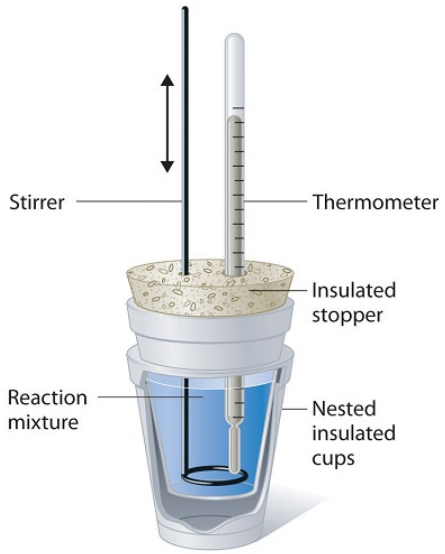


Figure 1.5.3: A Coffee-Cup Calorimeter. This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.

Before we practice calorimetry problems involving chemical reactions, consider a simpler example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium. If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter's surroundings. Under these ideal circumstances, the net heat change is zero:

[redacted]

This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

[redacted]

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that $q_{substance\ M}$ and $q_{substance\ W}$ are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either q value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described, $q_{substance\ M}$ is a negative value and $q_{\text{substance W}}$ is positive, since heat is transferred from M to W.

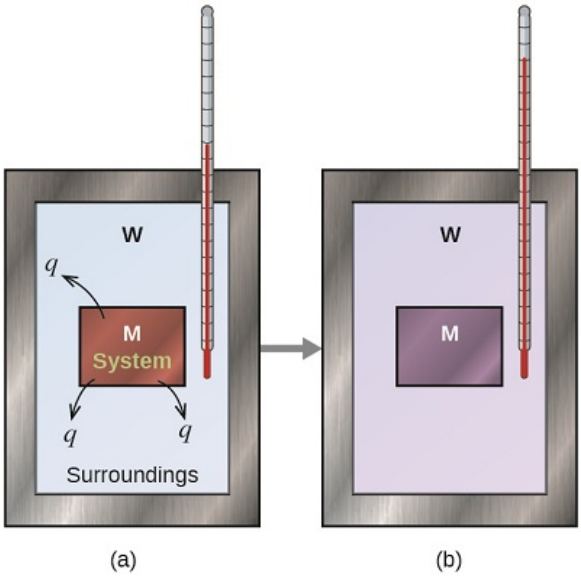


Figure 1.5.4: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Example 1.5.5: Heat between Substances at Different Temperatures

A 360-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water was measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table T4), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat "lost" to the surroundings, then heat given off by rebar = –heat taken in by water, or:

$$q_{\text{rebar}} = -q_{\text{water}}$$

Since we know how heat is related to other measurable quantities, we have:

$$(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}}$$

Letting f = final and i = initial, in expanded form, this becomes:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{\text{f,rebar}} - T_{\text{i,rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

$$(0.449\ \text{J/g °C})(360\text{g})(42.7\text{°C} - T_{\text{i,rebar}}) = -(4.184\ \text{J/g °C})(425\ \text{g})(42.7\text{°C} - 24.0\text{°C})$$

$$T_{\text{i,rebar}} = \frac{(4.184\ \text{J/g °C})(425\ \text{g})(42.7\text{°C} - 24.0\text{°C})}{(0.449\ \text{J/g °C})(360\ \text{g})} + 42.7\text{°C}$$

Solving this gives $T_{i,rebar}$= 248 °C, so the initial temperature of the rebar was 248 °C.

Exercise 1.5.5A

A 248-g piece of copper is dropped into 390 mL of water at 22.6 °C. The final temperature of the water was measured as 39.9 °C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

Answer

The initial temperature of the copper was 335.6 °C.

Exercise 1.5.5B

A 248-g piece of copper initially at 314 °C is dropped into 390 mL of water initially at 22.6 °C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

Answer

The final temperature (reached by both copper and water) is 38.8 °C.

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

Example 1.5.6: Identifying a Metal by Measuring Specific Heat

A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0 °C. The final temperature is 28.5 °C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.

Solution

Assuming perfect heat transfer, heat given off by metal = –heat taken in by water, or:

$$q_{\text{metal}} = -q_{\text{water}}$$

In expanded form, this is:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{\text{f,metal}} - T_{\text{i,metal}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0 °C; and that for water, 60.0 mL = 60.0 g; we have:

$$(c_{\text{metal}})(59.7\text{ g})(28.5°\text{C} - 100.0°\text{C}) = -(4.18\text{ J/g °C})(60.0\text{ g})(28.5°\text{C} - 22.0°\text{C})$$

Solving this:

$$c_{\text{metal}} = \frac{-(4.184\text{ J/g °C})(60.0\text{ g})(6.5°\text{C})}{(59.7\text{ g})(-71.5°\text{C})} = 0.38\text{ J/g °C}$$

Comparing this with values in Table T4, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

Exercise 1.5.6

A 92.9-g piece of a silver/gray metal is heated to 178.0 °C, and then quickly transferred into 75.0 mL of water initially at 24.0 °C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7 °C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

Answer

$$c_{metal} = 0.13 \ \ J/g \ \ ^\circ C$$

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the surroundings. Because energy is neither created nor destroyed during a chemical reaction, there is no overall energy change during the reaction. The heat produced or consumed in the reaction (the "system"), $q_{reaction}$, plus the heat absorbed or lost by the solution (the "surroundings"), $q_{solution}$, must add up to zero:

[redacted]

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

[redacted]

This concept lies at the heart of all calorimetry problems and calculations. Because the heat released or absorbed at constant pressure is equal to ΔH, the relationship between heat and ΔH_{rxn} is

[redacted]

The use of a constant-pressure calorimeter is illustrated in Example 1.5.7.

Example 1.5.7: Heat of Solution

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0°C to 34.7°C. The density of water in this temperature range averages 0.9969 g/cm^3. What is ΔH_{soln} (in kilojoules per mole)? Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

Given: mass of substance, volume of solvent, and initial and final temperatures

Asked for: ΔH_{soln}

Strategy:

A. Calculate the mass of the solution from its volume and density and calculate the temperature change of the solution.
B. Find the heat flow that accompanies the dissolution reaction by substituting the appropriate values into Equation 1.3.858 .
C. Use the molar mass of KOH to calculate ΔH_{soln}.

Solution:A

To calculate ΔH_{soln}, we must first determine the amount of heat released in the calorimetry experiment. The mass of the solution is

$$\left(100.0 \cancel{mL}\ \mathrm{H_2O}\right)\left(0.9969\ g/\cancel{mL}\right) + 5.03\ g\ KOH = 104.72\ g$$

The temperature change is (34.7°C – 23.0°C) = +11.7°C.

Solution B

Because the solution is not very concentrated (approximately 0.9 M), we assume that the specific heat of the solution is the same as that of water. The heat flow that accompanies dissolution is thus

$$\begin{aligned} q_{calorimater} &= mc_s\Delta T \\ &= \left(104.72\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^\circ C}}\right)\left(11.7\ \cancel{^\circ C}\right) \\ &= 5130\ J \\ &= 5.13\ kJ \end{aligned}$$

The temperature of the solution increased because heat was absorbed by the solution ($q > 0$). Where did this heat come from? It was released by KOH dissolving in water. From Equation 1.3.858, we see that

$$\Delta H_{rxn} = -q_{calorimeter} = -5.13\,kJ$$

This experiment tells us that dissolving 5.03 g of KOH in water is accompanied by the *release* of 5.13 kJ of energy. Because the temperature of the solution increased, the dissolution of KOH H in water must be exothermic.

C The last step is to use the molar mass of KOH to calculate ΔH_{soln} - the heat associated when dissolving 1 mol of KOH:

$$\begin{aligned} \Delta H_{soln} &= \left(\frac{5.13\ kJ}{5.03\ \cancel{g}}\right)\left(\frac{56.11\ \cancel{g}}{1\ mol}\right) \\ &= -57.2\ kJ/mol \end{aligned}$$

Exercise 1.5.7: Heat of Dissolving

A coffee-cup calorimeter contains 50.0 mL of distilled water at 22.7°C. Solid ammonium bromide (3.14 g) is added and the solution is stirred, giving a final temperature of 20.3°C. Using the same assumptions as in Example 1.5.7, find ΔH_{soln} for NH_4Br (in kilojoules per mole).

Answer

16.6 kJ/mol

Constant-Volume Calorimetry

Constant-pressure calorimeters are not very well suited for studying reactions in which one or more of the reactants is a gas, such as a combustion reaction. The enthalpy changes that accompany combustion reactions are therefore measured using a constant-volume calorimeter, such as the bomb calorimeter (A device used to measure energy changes in chemical processes. shown

schematically in Figure 1.5.4). The reactant is placed in a steel cup inside a steel vessel with a fixed volume (the “bomb”). The bomb is then sealed, filled with excess oxygen gas, and placed inside an insulated container that holds a known amount of water. Because combustion reactions are exothermic, the temperature of the bath and the calorimeter increases during combustion. If the heat capacity of the bomb and the mass of water are known, the heat released can be calculated.

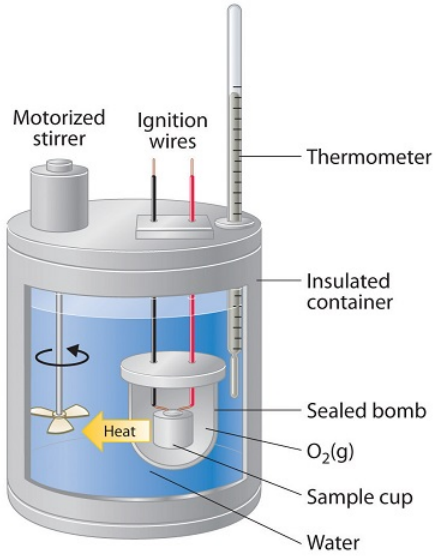


Figure 1.5.4: A Bomb Calorimeter. After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction. (CC BY-SA-NC; anonymous)

Because the volume of the system (the inside of the bomb) is fixed, the combustion reaction occurs under conditions in which the volume, but not the pressure, is constant. The heat released by a reaction carried out at constant volume is identical to the change in *internal energy* (ΔU) rather than the enthalpy change (ΔH); ΔU is related to ΔH by an expression that depends on the change in the number of moles of gas during the reaction. The difference between the heat flow measured at constant volume and the enthalpy change is usually quite small, however (on the order of a few percent). Assuming that $\Delta U < \Delta H$, the relationship between the measured temperature change and ΔH_{comb} is given in Equation 1.5.883, where C_{bomb} is the total heat capacity of the steel bomb and the water surrounding it

[redacted]

To measure the heat capacity of the calorimeter, we first burn a carefully weighed mass of a standard compound whose enthalpy of combustion is accurately known. Benzoic acid ($C_6H_5CO_2H$) is often used for this purpose because it is a crystalline solid that can be obtained in high purity. The combustion of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat per gram (i.e., its ΔH_{comb} = −26.38 kJ/g). This value and the measured increase in temperature of the calorimeter can be used to determine C_{bomb}. The use of a bomb calorimeter to measure the ΔH_{comb} of a substance is illustrated in Example 1.5.8.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

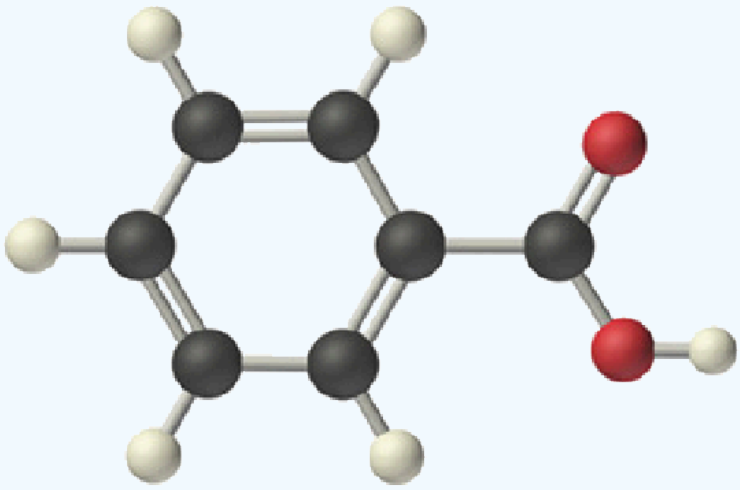
View this YouTube Video online

https://www.youtube.com/embed/RJXq92dzAWA?vq=hd1080

Video 1.5.1***:*** *Video of view how a bomb calorimeter is prepared for action.*

Example 1.5.8: Combustion of Glucose

The combustion of 0.579 g of benzoic acid in a bomb calorimeter caused a 2.08°C increase in the temperature of the calorimeter. The chamber was then emptied and recharged with 1.732 g of glucose and excess oxygen. Ignition of the glucose resulted in a temperature increase of 3.64°C. What is the ΔH_{comb} of glucose?



Benzoic acid

Given: mass and ΔT for combustion of standard and sample

Asked for: ΔH_{comb} of glucose

Strategy:

A. Calculate the value of q_{rxn} for benzoic acid by multiplying the mass of benzoic acid by its ΔH_{comb}. Then use Equation 1.3.858 to determine the heat capacity of the calorimeter (C_{bomb}) from q_{comb} and ΔT.
B. Calculate the amount of heat released during the combustion of glucose by multiplying the heat capacity of the bomb by the temperature change. Determine the ΔH_{comb} of glucose by multiplying the amount of heat released per gram by the molar mass of glucose.

Solution:

Step A: The first step is to use Equation 1.3.858 and the information obtained from the combustion of benzoic acid to calculate C_{bomb}. We are given ΔT, and we can calculate q_{comb} from the mass of benzoic acid:

$$q_{comb} = \left(0.579 \cancel{g}\right)\left(-26.38\ kJ/\cancel{g}\right) = -15.3\ kJ$$

From Equation 1.3.858,

$$-C_{bomb} = \frac{q_{comb}}{\Delta T} = \frac{-15.3\ kJ}{2.08\ ^oC} = -7.34\ kJ/^oC$$

Step B: According to the strategy, we can now use the heat capacity of the bomb to calculate the amount of heat released during the combustion of glucose:

$$q_{comb} = -C_{bomb}\Delta T = (-7.34\ kJ/^oC)\,(3.64\ ^oC) = -26.7\ kJ$$

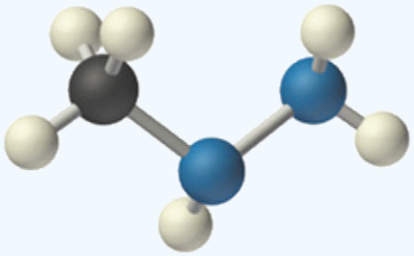
Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the ΔH_{comb} of glucose is

$$\Delta H_{comb} = \left(\frac{-26.7\ kJ}{1.732\ \cancel{g}}\right)\left(\frac{180.16\ \cancel{g}}{mol}\right) = -2780\ kJ/mol = 2.78 \times 10^3\ kJ/mol$$

This result is in good agreement (< 1% error) with the value of $\Delta H_{comb} = -2803\ kJ/mol$ that calculated using enthalpies of formation.

Exercise 1.5.8: Combustion of Benzoic Acid

When 2.123 g of benzoic acid is ignited in a bomb calorimeter, a temperature increase of 4.75°C is observed. When 1.932 g of methylhydrazine (CH_3NHNH_2) is ignited in the same calorimeter, the temperature increase is 4.64°C. Calculate the ΔH_{comb} of methylhydrazine, the fuel used in the maneuvering jets of the US space shuttle.



Methylhydrazine

Answer

-1.30×10^3 kJ/mol

Summary

Calorimetry measures enthalpy changes during chemical processes, where the magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. **Calorimetry** is the set of techniques used to measure enthalpy changes during chemical processes. It uses devices called *calorimeters*, which measure the change in temperature when a chemical reaction is carried out. The magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. The **heat capacity (*C*)** of an object is the amount of energy needed to raise its temperature by 1°C; its units are joules per degree Celsius. The **specific heat** (c_s) of a substance is the amount of energy needed to raise the temperature of 1 g of the substance by 1°C, and the **molar heat capacity** (c_p) is the amount of energy needed to raise the temperature of 1 mol of a substance by 1°C. Liquid water has one of the highest specific heats known. Heat flow measurements can be made with either a **constant-pressure calorimeter**, which gives ΔH values directly, or a **bomb calorimeter**, which operates at constant volume and is particularly useful for measuring enthalpies of combustion.

Thermal energy itself cannot be measured easily, but the temperature change caused by the flow of thermal energy between objects or substances can be measured. Calorimetry describes a set of techniques employed to measure enthalpy changes in chemical processes using devices called *calorimeters*. To have any meaning, the quantity that is actually measured in a calorimetric experiment, the change in the temperature of the device, must be related to the heat evolved or consumed in a chemical reaction. We begin this section by explaining how the flow of thermal energy affects the temperature of an object.

Contributors and Attributions

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1.6: Molecules as Energy Carriers and Converters

Learning Objectives

Make sure you thoroughly understand the following essential concepts:

- Describe the sources of potential energy and kinetic energy contained in a molecule.
- Describe the nature of "*thermal*" *energy*, and how it relates to other forms of kinetic energy and to *temperature*.
- Explain why the simplest molecules (monatomic and diatomic) have smaller heat capacities than polyatomic molecules.
- Similarly, explain why the dependence of heat capacity on the temperature is different for monatomic and polyatomic molecules.

All molecules at temperatures above absolute zero possess *thermal energy*— the randomized kinetic energy associated with the various motions the molecules as a whole, and also the atoms within them, can undergo. Polyatomic molecules also possess *potential energy* in the form of chemical bonds. Molecules are thus both vehicles for **storing and transporting energy**, and the means of **converting it from one form to another** when the formation, breaking, or rearrangement of the chemical bonds within them is accompanied by the uptake or release of *heat*.

Internal Energy: Potential + Kinetic

Chemical substances are made of atoms, or more generally, of positively charged nuclei surrounded by negatively charged electrons. A molecule such as dihydrogen, H_2, is held together by electrostatic attractions mediated by the electrons shared between the two nuclei. The total potential energy of the molecule is the sum of the repulsions between like charges and the attractions between electrons and nuclei:

[redacted]

In other words, the potential energy of a molecule depends on the time-averaged relative locations of its constituent nuclei and electrons. This dependence is expressed by the familiar potential energy curve which serves as an important description of the chemical bond between two atoms.

- ***Translation*** refers to movement of an object as a complete unit. Translational motions of molecules in solids or liquids are restricted to very short distances comparable to the dimensions of the molecules themselves, whereas in gases the molecules typically travel hundreds of molecular diameters between collisions. In gaseous hydrogen, for example, the molecules will be moving freely from one location to another; this is called *translational motion*, and the molecules therefore possess *translational kinetic energy*

$$KE_{trans} = \frac{mv^2}{2} \tag{1.6.1408}$$

  in which v stands for the average velocity of the molecules; you may recall from your study of gases that v, and therefore KE_{trans}, depends on the temperature.

In addition to translation, molecules composed of two or more atoms can possess other kinds of motion.

- Because a chemical bond acts as a kind of spring, the two atoms in H_2 will have a natural ***vibrational frequency***. In more complicated molecules, many different modes of vibration become possible, and these all contribute a vibrational term KE_{vib} to the total kinetic energy.
- Finally, a molecule can undergo ***rotational*** motions which give rise to a third term KE_{rot}.

Thus the total kinetic energy of a molecule is the sum

[redacted]

The total energy of the molecule (i.e, its *internal energy* U) is just the sum of total kinetic and potential energies:

Although Equation 1.6.887 is simple and straightforward, it cannot take us very far in understanding and predicting the behavior of even one molecule, let alone a large number of them. The reason, of course, is the chaotic and unpredictable nature of molecular motion. Fortunately, the behavior of a large collection of molecules, like that of a large population of people, can be described by statistical methods.

How Molecules "Store" Thermal Energy

As noted previously, the *heat capacity* of a substance is a measure of how sensitively its temperature is affected by a change in heat content; the greater the heat capacity, the less effect a given flow of heat q will have on the temperature.

Thermal energy is randomized kinetic energy and temperature is a measure of it.

For monatomic gases, temperature is a measure of the average kinetic energy due to *translational motions* of molecules. If vibrational or rotational motions are also active (e.g., diatomic gases), these motions will also accept thermal energy and reduce the amount that goes into translational motions. Because the temperature depends only on the latter, the effect of the other kinds of motions will be to reduce the dependence of the internal energy on the temperature, thus raising the *heat capacity* of a substance.

Table 1.6.1: Molar heat capacities (kJ mol^{-1} K^{-1}) of some gaseous substances at constant pressure.

monatomic		diatomic		triatomic	
He	20.5	CO	29.3	H_2O	33.5
Ne	20.5	N_2	29.5	D_2O	34.3
Ar	20.5	F_2	31.4	CO_2	37.2
Kr	20.5	Cl_2	33.9	CS_2	45.6

Whereas monatomic molecules can only possess translational thermal energy, two additional kinds of motions become possible in polyatomic molecules. A linear molecule has an axis that defines two perpendicular directions in which rotations can occur; each represents an additional *degree of freedom*, so the two together contribute a total of ½ *R* to the heat capacity.

Vibrational and rotational motions are not possible for monatomic species such as the noble gas elements, so these substances have the lowest heat capacities. Moreover, as you can see in the leftmost column of Table 1.6.1, their heat capacities are all the same. This reflects the fact that translational motions are the same for all particles; all such motions can be resolved into three directions in space, each contributing one *degree of freedom* to the molecule and $\frac{1}{2}R$ to its heat capacity (Equation 1.6.888) where R is the gas constant, $8.314\ J\ K^{-1}$.

Think of a "degree of freedom" as a motion that contributes to the total kinetic energy of a molecule.

For a non-linear molecule, *rotations* are possible along all three directions of space, so these molecules have a rotational heat capacity of $3/2R$.

Linear molecules can only rotate in two dimensions so rotational motions in linear molecules contribute less than rotational motions in nonlinear molecules to the heat capacity.

Finally, the individual atoms within a molecule can move relative to each other, producing a *vibrational motion*. A nonlinear molecule consisting of N atoms can vibrate in $3N-6$ different ways or modes, while a linear molecule has $3N-5$ modes. Each vibrational mode contributes R (rather than ½ *R*) to the total heat capacity (these results come from advanced mechanics and will not be proven here).

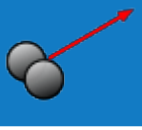
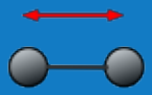
and

The total heat capacity of a mole of gas molecules is then

$$C_p = C_{trans} + C_{rot} + C_{vib} \tag{1.6.1409}$$

which differs based on the geometry and number of atoms in the molecule considered (Equations 9.5.729 - 1.6.891) as shown in Table 1.6.2.

Table 1.6.2: Contribution of molecular motions to heat capacity

type of motion →	translation 	Rotation 	vibration 
monatomic	$3/2R$	0	0
diatomic	$3/2R$	R	R ($N = 2$ in Equation 1.6.890)
polyatomic	$3/2R$	$3/2R$(nonlinear) or R (linear)	$(3N–6)R$ (nonlinear) or $(3N–5)R$ (linear)
separation between adjacent levels, (kJ mol^{-1})	6.0 × 10^{-17} J (O_2)	373 J (HCl)	26,000 J (HCl)

Now we are in a position to understand why more complicated molecules have higher heat capacities. The total kinetic energy of a molecule is the sum of those due to the various kinds of motions:

When a monatomic gas absorbs heat, all of the energy ends up in translational motion, and thus goes to increase its temperature. In a polyatomic gas, by contrast, the absorbed energy is partitioned among the other kinds of motions; since only the translational motions contribute to the temperature, the temperature rise is smaller, and thus the heat capacity is larger. There is one very significant complication, however: classical mechanics predicts that the energy is always partitioned equally between all degrees of freedom. Experiments, however, show that this is observed only at quite high temperatures. The reason is that these motions are all *quantized*. This means that only certain increments of energy are possible for each mode of motion, and unless a certain minimum amount of energy is available, a given mode will not be active at all and will contribute nothing to the heat capacity.

Translational Energy Levels are Effectively Continuous

The shading in Figure 1.6.1 indicates the average thermal energy available at 300 K. Only those levels within this range will have significant occupancy as indicated by the thickness of the lines in the two rightmost columns. At 300 K, only the lowest vibrational states and the first few rotational states will be active. Most of the thermal energy will be confined to the translational levels whose minute spacing (10^{-17} J) causes them to appear as a continuum although technically quantized (by the particle in a box quantum model).

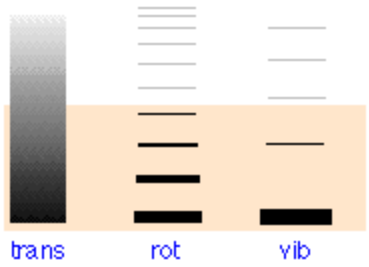


Figure 1.6.1: Different energy levels associated with translation, rotation, and vibration compared to an arbitrary thermal energy (tan level).

Heat capacity of dihydrogen as a function of temperature. Figure 1.6.2 is typical of those for other polyatomic molecules, and shows the practical consequences of the spacings of the various forms of thermal energy. Thus translational motions are available at virtually all temperatures, but contributions to heat capacity by rotational or vibrational motions can only develop at temperatures sufficiently large to excite these motions.

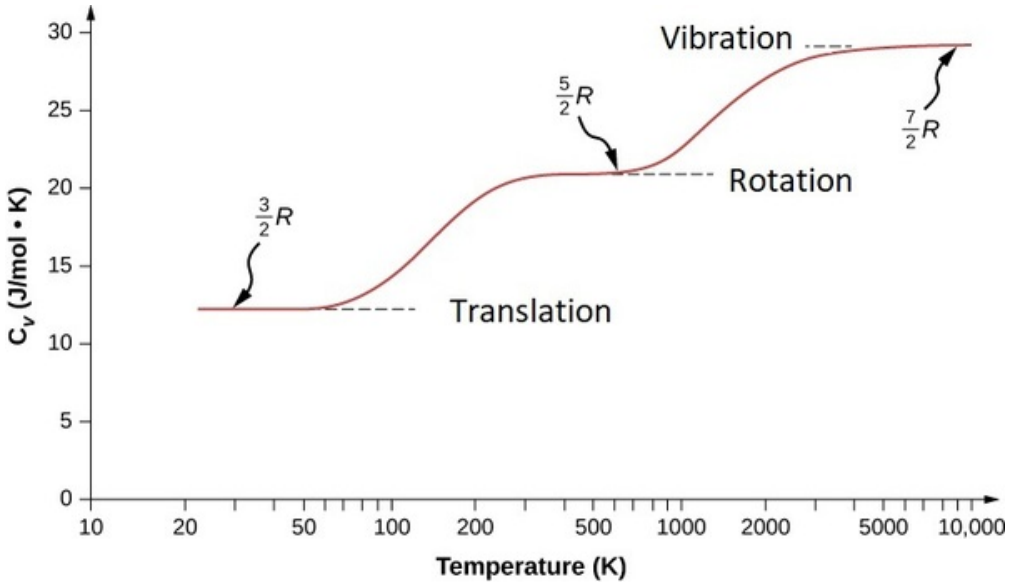


Figure 1.6.2: The molar heat capacity of hydrogen as a function of temperature (on a logarithmic scale). The three "steps" or "plateaus" show different numbers of degrees of freedom that the typical energies of molecules must achieve to activate. Translational kinetic energy corresponds to three degrees of freedom, rotational to another two, and vibrational to yet another two. (CC BY 4.0; OpenStax).

It turns out that translational energy levels are spaced so closely that these motions are active almost down to absolute zero, so all gases possess a heat capacity of at least 3/2 *R* at all temperatures. Rotational motions do not get started until intermediate temperatures, typically 300-500K, so within this range heat capacities begin to increase with temperature. Finally, at very high temperatures, vibrations begin to make a significant contribution to the heat capacity

The strong intermolecular forces of liquids and many solids allow heat to be channeled into vibrational motions involving more than a single molecule, further increasing heat capacities. One of the well known "anomalous" properties of liquid water is its high heat capacity (75 J mol^{-1} K^{-1}) due to intermolecular hydrogen bonding, which is directly responsible for the moderating influence of large bodies of water on coastal climates.

Heat capacities of metals

Metallic solids are a rather special case. In metals, the atoms oscillate about their equilibrium positions in a rather uniform way which is essentially the same for all metals, so they should all have about the same heat capacity. We can model the atoms of a solid as attached to neighboring atoms by springs (Figure 1.6.3).

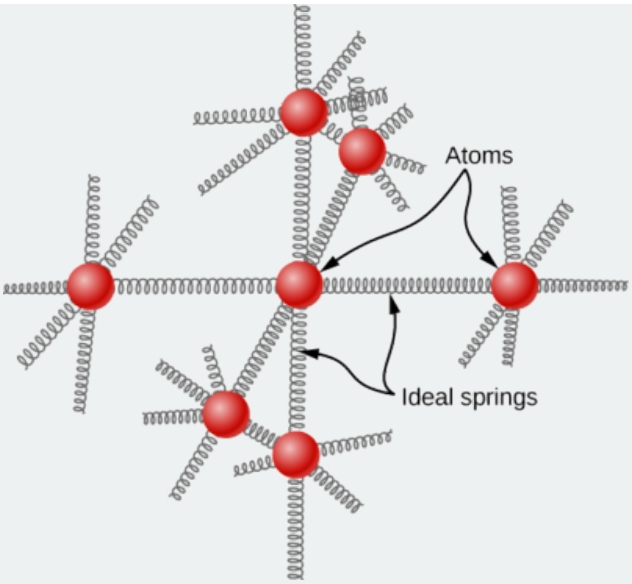


Figure 1.6.3: In a simple model of a solid element, each atom is attached to others by six springs, two for each possible motion: x, y, and z. Each of the three motions corresponds to two degrees of freedom, one for kinetic energy and one for potential energy. (CC BY-SA 4.0; OpenStax).

Analogously to the discussion of vibration in the previous module, each atom has six degrees of freedom: one kinetic and one potential for each of the *x*-, *y*-, and *z*-directions. Accordingly, the molar specific heat of a metal should be $3R$. This result, known as the *Law of Dulong and Petit*, works fairly well experimentally at room temperature. In the 19th century these workers discovered that the molar heat capacities of all the metallic elements they studied were around to 25 J mol^{-1} K^{-1}, which is close to what classical physics predicts for crystalline metals. This observation played an important role in characterizing new elements, for it provided a means of estimating their molar masses by a simple heat capacity measurement.

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1.7: Heats of Reactions - ΔU and ΔH

Learning Objectives

- To understand how enthalpy pertains to chemical reactions

When we study energy changes in chemical reactions, the most important quantity is usually the enthalpy of reaction (ΔH_{rxn}), the change in enthalpy that occurs during a reaction (such as the dissolution of a piece of copper in nitric acid). If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH_{rxn} is negative. Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH_{rxn} is positive. Thus $\Delta H_{rxn} < 0$ *for an exothermic reaction*, and $\Delta H_{rxn} > 0$ *for an endothermic reaction*. In chemical reactions, bond breaking requires an input of energy and is therefore an endothermic process, whereas bond making releases energy, which is an exothermic process. The sign conventions for heat flow and enthalpy changes are summarized in the following table:

Reaction Type	q	ΔH_{rxn}
exothermic	< 0	< 0 (heat flows from a system to its surroundings)
endothermic	> 0	> 0 (heat flows from the surroundings to a system)

If ΔH_{rxn} is negative, then the enthalpy of the products is less than the enthalpy of the reactants; that is, *an exothermic reaction is energetically downhill* (Figure $1.7.1a$). Conversely, if ΔH_{rxn} is positive, then the enthalpy of the products is greater than the enthalpy of the reactants; thus, *an endothermic reaction is energetically uphill* (Figure $1.7.1b$).

Bond breaking **ALWAYS** requires an input of energy; bond making **ALWAYS** releases energy.

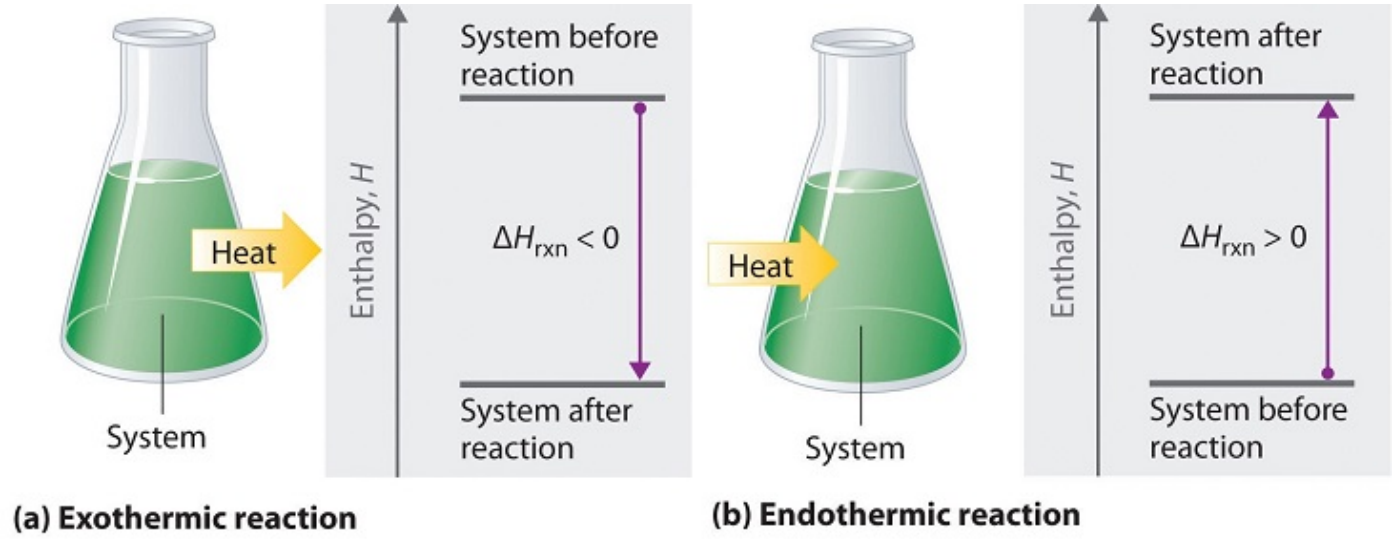


Figure $1.7.1$: The Enthalpy of Reaction. Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH_{rxn} is negative, and the reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, ΔH_{rxn} is positive, and the reaction is endothermic; it is energetically uphill.

Two important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

- **Reversing a reaction or a process changes the sign of ΔH.** Ice *absorbs* heat when it melts (electrostatic interactions are broken), so liquid water must *release* heat when it freezes (electrostatic interactions are formed):

[redacted]

In both cases, the *magnitude* of the enthalpy change is the same; only the *sign* is different.

- **Enthalpy is an extensive property (like mass).** The magnitude of ΔH for a reaction is proportional to the amounts of the substances that react. For example, a large fire produces more heat than a single match, even though the chemical reaction—the combustion of wood—is the same in both cases. For this reason, the enthalpy change for a reaction is usually given in kilojoules per mole of a particular reactant or product. Consider Equation 1.7.896, which describes the reaction of aluminum with iron(III) oxide (Fe_2O_3) at constant pressure. According to the reaction stoichiometry, 2 mol of Fe, 1 mol of Al_2O_3, and 851.5 kJ of heat are produced for every 2 mol of Al and 1 mol of Fe_2O_3 consumed:

[redacted]

Thus $\Delta H = -851.5\ kJ/mol$ of $\mathrm{Fe_2O_3}$. We can also describe ΔH for the reaction as –425.8 kJ/mol of Al: because 2 mol of Al are consumed in the balanced chemical equation, we divide –851.5 kJ by 2. When a value for ΔH, in kilojoules rather than kilojoules per mole, is written after the reaction, as in Equation 1.7.896, it is the value of Δ*H* corresponding to the reaction of the molar quantities of reactants as given in the balanced chemical equation:

[redacted]

If 4 mol of Al and 2 mol of Fe_2O_3 react, the change in enthalpy is 2 × (–851.5 kJ) = –1703 kJ. We can summarize the relationship between the amount of each substance and the enthalpy change for this reaction as follows:

[redacted]

The relationship between the magnitude of the enthalpy change and the mass of reactants is illustrated in Example 1.7.1.

1.7.1 Exam

Certain parts of the world, such as southern California and Saudi Arabia, are short of fresh water for drinking. One possible solution to the problem is to tow icebergs from Antarctica and then melt them as needed. If ΔH is 6.01 kJ/mol for the reaction $\mathrm{H_2O\,(s) \longrightarrow H_2O\,(l)}$ at 0°C and constant pressure, how much energy would be required to melt a moderately large iceberg with a mass of 1.00 million metric tons (1.00×10^6 metric tons)? (A metric ton is 1000 kg.)

Given: energy per mole of ice and mass of iceberg

Asked for: energy required to melt iceberg

Strategy:

A. Calculate the number of moles of ice contained in 1 million metric tons (1.00×10^6 metric tons) of ice.
B. Calculate the energy needed to melt the ice by multiplying the number of moles of ice in the iceberg by the amount of energy required to melt 1 mol of ice.

Solution A

Because enthalpy is an extensive property, the amount of energy required to melt ice depends on the amount of ice present. We are given Δ*H* for the process—that is, the amount of energy needed to melt 1 mol (or 18.015 g) of ice—so we need to calculate the number of moles of ice in the iceberg and multiply that number by Δ*H* (+6.01 kJ/mol):

$$moles\ H_2O = 1.00 \times 10^6\ \cancel{metric\ tons}\ H_2O \left(\frac{1000\ \cancel{kg}}{1\ \cancel{metric\ ton}}\right)\left(\frac{1000\ \cancel{g}}{1\ \cancel{kg}}\right)\left(\frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}}\right)$$

$$= 5.55 \times 10^{10}\ mol H_2O$$

Solution B

he energy needed to melt the iceberg is thus

$$\left(\frac{6.01\ kJ}{\cancel{mol\ H_2O}}\right)\left(5.55 \times 10^{10}\ \cancel{mol\ H_2O}\right) = 3.34 \times 10^{11}\ kJ$$

Because so much energy is needed to melt the iceberg, this plan would require a relatively inexpensive source of energy to be practical. To give you some idea of the scale of such an operation, the amounts of different energy sources equivalent to the amount of energy needed to melt the iceberg are shown in the table below.

Possible sources of the approximately 3.34 × 10^{11} kJ needed to melt a 1.00 × 10^{6} metric ton iceberg

- Combustion of 3.8 × 10^{3} ft^{3} of natural gas
- Combustion of 68,000 barrels of oil
- Combustion of 15,000 tons of coal
- 1.1 × 10^{8} kilowatt-hours of electricity

1.7.1Exerc

If 17.3 g of powdered aluminum are allowed to react with excess $\mathrm{Fe_2O_3}$, how much heat is produced?

Answer

- 273 kJ

Types of Enthalpies of Reactions

One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, such as the following:

- **Enthalpy of combustion** (ΔH_{comb}) is the change in enthalpy that occurs during a combustion reaction. Enthalpy changes have been measured for the combustion of virtually any substance that will burn in oxygen; these values are usually reported as the enthalpy of combustion per mole of substance.
- **Enthalpy of fusion** (ΔH_{fus}) is the enthalpy change that accompanies the melting (fusion) of 1 mol of a substance. The enthalpy change that accompanies the melting, or fusion, of 1 mol of a substance; these values have been measured for almost all the elements and for most simple compounds.
- **Enthalpy of vaporization** (ΔH_{vap}) is the enthalpy change that accompanies the vaporization of 1 mol of a substance. The enthalpy change that accompanies the vaporization of 1 mol of a substance; these values have also been measured for nearly all the elements and for most volatile compounds.
- **Enthalpy of solution** (ΔH_{soln}) is the change in enthalpy that occurs when a specified amount of solute dissolves in a given quantity of solvent.

Table 1.7.1: Enthalpies of Vaporization and Fusion for Selected Substances at Their Boiling Points and Melting Points

Substance	ΔH_{vap} (kJ/mol)	ΔH_{fus} (kJ/mol)
argon (Ar)	6.3	1.3
methane (CH_4)	9.2	0.84
ethanol (CH_3CH_2OH)	39.3	7.6
benzene (C_6H_6)	31.0	10.9
water (H_2O)	40.7	6.0
mercury (Hg)	59.0	2.29
iron (Fe)	340	14

The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

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https://www.youtube.com/embed/z2KUaIEF9qI?vq=hd1080

Enthalpy of Reaction: https://youtu.be/z2KUaIEF9qI

Summary

Enthalpy is a state function used to measure the heat transferred from a system to its surroundings or vice versa at constant pressure. Only the **change in enthalpy** (ΔH) can be measured. A negative ΔH means that heat flows from a system to its surroundings; a positive ΔH means that heat flows into a system from its surroundings. For a chemical reaction, the **enthalpy of reaction** (ΔH_{rxn}) is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}.

The magnitude of ΔH_{rxn} also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion** (ΔH_{fus}) and the **enthalpy of vaporization** (ΔH_{vap}), respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for

the individual reactions, which is **Hess's law**. The **enthalpy of combustion** (ΔH_{comb}) is the enthalpy change that occurs when a substance is burned in excess oxygen.

Contributors and Attributions

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1.8: Indirect Determination of ΔH - Hess's Law

Learning Objectives

- To use Hess's law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

Because enthalpy is a state function, the enthalpy change for a reaction depends on only two things:

1. the masses of the reacting substances and
2. the physical states of the reactants and products.

It does **not** depend on the path by which reactants are converted to products. If you climbed a mountain, for example, the altitude change would not depend on whether you climbed the entire way without stopping or you stopped many times to take a break. If you stopped often, the overall change in altitude would be the sum of the changes in altitude for each short stretch climbed. Similarly, when we add two or more balanced chemical equations to obtain a net chemical equation, ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This principle is called Hess's law, after the Swiss-born Russian chemist Germain Hess (1802–1850), a pioneer in the study of thermochemistry. Hess's law allows us to calculate ΔH values for reactions that are difficult to carry out directly by adding together the known ΔH values for individual steps that give the overall reaction, even though the overall reaction may not actually occur via those steps.

We can illustrate Hess's law using the thermite reaction. The overall reaction shown in Equation 1.8.899 can be viewed as occurring in three distinct steps with known ΔH values. As shown in Figure 1.8.1:

1. The first reaction produces 1 mol of solid aluminum oxide ($\mathrm{Al_2O_3}$) and 2 mol of liquid iron at its melting point of 1758°C (Equation 1.8.899a); the enthalpy change for this reaction is –732.5 kJ/mol of $\mathrm{Fe_2O_3}$.
2. The second reaction is the conversion of 2 mol of liquid iron at 1758°C to 2 mol of solid iron at 1758°C (Equation 1.8.899b); the enthalpy change for this reaction is –13.8 kJ/mol of Fe (–27.6 kJ per 2 mol Fe).
3. In the third reaction, 2 mol of solid iron at 1758°C is converted to 2 mol of solid iron at 25°C (Equation 1.8.899c); the enthalpy change for this reaction is –45.5 kJ/mol of Fe (–91.0 kJ per 2 mol Fe).

As you can see in Figure 1.8.1, the overall reaction is given by the longest arrow (shown on the left), which is the sum of the three shorter arrows (shown on the right). Adding Equations 1.8.899a-1.8.899c} gives the overall reaction, shown Equation 1.8.899d:



By Hess's law, the enthalpy change for part (d) is the sum of the enthalpy changes for parts (a), (b), and (c). In essence, Hess's law enables us to calculate the enthalpy change for the sum of a series of reactions without having to draw a diagram like that in Figure 1.8.1.

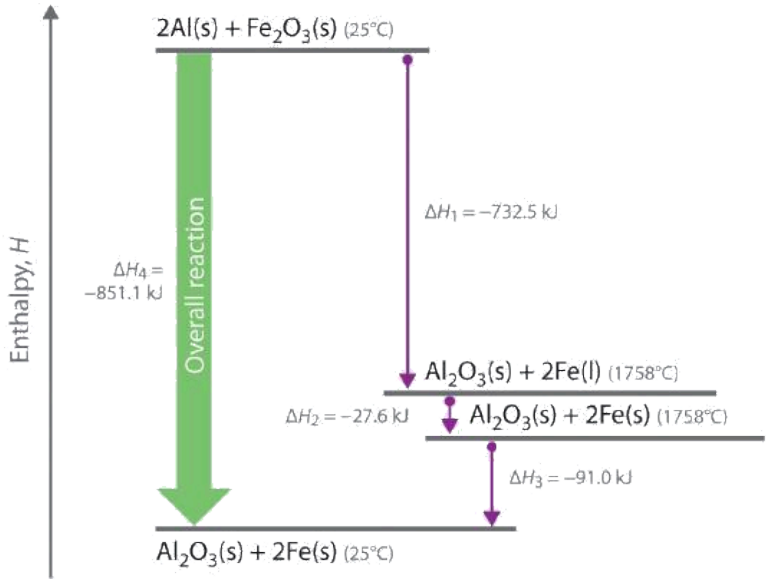


Figure 1.8.1: Energy Changes Accompanying the Thermite Reaction. Because enthalpy is a state function, the overall enthalpy change for the reaction of 2 mol of Al(s) with 1 mol of Fe_2O_3(s) is −851.1 kJ, whether the reaction occurs in a single step (ΔH_4, shown on the left) or in three hypothetical steps (shown on the right) that involve the successive formation of solid Al_2O_3 and liquid iron (ΔH_1), solid iron at 1758°C (ΔH_2), and solid iron at 25°C (ΔH_3). Thus $\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$, as stated by Hess's law.

Comparing parts (a) and (d) in Equation 1.8.899 also illustrates an important point: The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution). When the product is liquid iron at its melting point (part (a) in Equation 1.8.899), only 732.5 kJ of heat are released to the surroundings compared with 852 kJ when the product is solid iron at 25°C (part (d) in Equation 1.8.899). The difference, 120 kJ, is the amount of energy that is released when 2 mol of liquid iron solidifies and cools to 25°C. It is important to specify the physical state of all reactants and products when writing a thermochemical equation.

When using Hess's law to calculate the value of ΔH for a reaction, follow this procedure:

1. Identify the equation whose ΔH value is unknown and write individual reactions with known ΔH values that, when added together, will give the desired equation. We illustrate how to use this procedure in Example 1.8.1.
2. Arrange the chemical equations so that the reaction of interest is the sum of the individual reactions.
3. If a reaction must be reversed, change the sign of ΔH for that reaction. Additionally, if a reaction must be multiplied by a factor to obtain the correct number of moles of a substance, multiply its ΔH value by that same factor.
4. Add together the individual reactions and their corresponding ΔH values to obtain the reaction of interest and the unknown ΔH.

Example 1.8.1

When carbon is burned with limited amounts of oxygen gas (O_2), carbon monoxide (CO) is the main product:

[redacted]

When carbon is burned in excess O_2, carbon dioxide (CO_2) is produced:

[redacted]

Use this information to calculate the enthalpy change per mole of CO for the reaction of CO with O_2 to give CO_2.

Given: two balanced chemical equations and their ΔH values

Asked for: enthalpy change for a third reaction

Strategy:

A. After balancing the chemical equation for the overall reaction, write two equations whose ΔH values are known and that, when added together, give the equation for the overall reaction. (Reverse the direction of one or more of the equations as necessary, making sure to also reverse the sign of ΔH.)
B. Multiply the equations by appropriate factors to ensure that they give the desired overall chemical equation when added together. To obtain the enthalpy change per mole of CO, write the resulting equations as a sum, along with the enthalpy change for each.

Solution:

A We begin by writing the balanced chemical equation for the reaction of interest:

[redacted]

There are at least two ways to solve this problem using Hess's law and the data provided. The simplest is to write two equations that can be added together to give the desired equation and for which the enthalpy changes are known. Observing that CO, a reactant in reaction 2 and a product in Equation reaction 1, we can reverse reaction 1 to give

$$2CO\,(g) \rightarrow 2C\,(s) + O_2\,(g) \qquad \Delta H = +221.0\ kJ$$

Because we have reversed the direction of the reaction, the sign of ΔH is changed. We can use reaction 2, as written because its product, CO_2, is the product we want in reaction 3,:

$$\mathrm{C\,(s) + O_2\,(g) \longrightarrow CO_2\,(s)} \qquad \Delta H = -393.5\ kJ \tag{1.8.1410}$$

B Adding these two equations together does not give the desired reaction, however, because the numbers of C(s) on the left and right sides do not cancel. According to our strategy, we can multiply the second equation by 2 to obtain 2 mol of C(s) as the reactant:

$$\mathrm{2\,C\,(s) + 2\,O_2\,(g) \longrightarrow 2\,CO_2\,(s)} \qquad \Delta H = -787.0\ kJ \tag{1.8.1411}$$

Writing the resulting equations as a sum, along with the enthalpy change for each, gives

$$\begin{array}{rcl} 2CO\,(g) & \rightarrow & \cancel{2C\,(s)} + \cancel{O_2\,(g)} \quad \Delta H = -\Delta H_1 = +221.0\ kJ \\ \cancel{2C\,(s)} + \cancel{2}\,O_2\,(g) & \rightarrow & 2CO_2\,(g) \quad \Delta H = -\Delta 2H_2 = -787.0\ kJ \\ 2CO\,(g) + O_2\,(g) & \rightarrow & 2CO_2\,(g) \quad \Delta H = -566.0\ kJ \end{array} \tag{1.8.1412}$$

Note that the overall chemical equation and the enthalpy change for the reaction are both for the reaction of 2 mol of CO with $\mathrm{O_2}$, and the problem asks for the amount per mole of CO. Consequently, we must divide both sides of the final equation and the magnitude of ΔH by 2:

$$CO\,(g) + \tfrac{1}{2}O_2\,(g) \rightarrow CO_2\,(g) \quad \Delta H = -283.0\ kJ$$

An alternative and equally valid way to solve this problem is to write the two given equations as occurring in steps. Note that we have multiplied the equations by the appropriate factors to allow us to cancel terms:

$$\begin{array}{lrcl} (A) & 2C\,(s) + O_2\,(g) & \rightarrow & \cancel{2CO\,(g)} \quad \Delta H_A = \Delta H_1 = +221.0\ kJ \\ (B) & \cancel{2CO\,(g)} + O_2\,(g) & \rightarrow & 2CO_2\,(g) \quad \Delta H_B = ? \\ (C) & 2C\,(s) + 2O_2\,(g) & \rightarrow & 2CO_2\,(g) \quad \Delta H = 2\Delta H_2 = 2 \times (-393.5\ kJ) = -787.0\ kJ \end{array} \tag{1.8.1413}$$

The sum of reactions A and B is reaction C, which corresponds to the combustion of 2 mol of carbon to give CO_2. From Hess's law, $\Delta H_A + \Delta H_B = \Delta H_C$, and we are given ΔH for reactions A and C. Substituting the appropriate values gives

$$-221.0\ kJ + \Delta H_B = -787.0\ kJ$$
$$\Delta H_B = -566.0$$

This is again the enthalpy change for the conversion of 2 mol of CO to CO_2. The enthalpy change for the conversion of 1 mol of CO to CO_2 is therefore –566.0 ÷ 2 = –283.0 kJ/mol of CO, which is the same result we obtained earlier. As you can see, there may be more than one correct way to solve a problem.

Exercise 1.8.1

The reaction of acetylene (C_2H_2) with hydrogen (H_2) can produce either ethylene (C_2H_4) or ethane (C_2H_6):

$$C_2H_2\,(g) + H_2\,(g) \rightarrow C_2H_4\,(g) \quad \Delta H = -175.7\ kJ/mol\ C_2H_2$$
$$C_2H_2\,(g) + 2H_2\,(g) \rightarrow C_2H_6\,(g) \quad \Delta H = -312.0\ kJ/mol\ C_2H_2$$

What is ΔH for the reaction of C_2H_4 with H_2 to form C_2H_6?

Answer

–136.3 kJ/mol of C_2H_4

Summary

Hess's law is that the overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions. For a chemical reaction, the **enthalpy of reaction** (ΔH_{rxn}) is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}.

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1.9: Standard Enthalpies of Formation

Learning Objectives

- To understand Enthalpies of Formation and be able to use them to calculate Enthalpies of Reaction

One way to report the heat absorbed or released by chemical reactions would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, starting from the elemental forms of each atom at 25 °C and 1 atm pressure.

Enthalpy of formation (ΔH_f) is the enthalpy change for the formation of 1 mol of a compound from its component elements, such as the formation of carbon dioxide from carbon and oxygen. The formation of any chemical can be as a reaction from the corresponding elements:

$$\text{elements} \rightarrow \text{compound}$$

which in terms of the the Enthalpy of formation becomes

[redacted]

For example, consider the combustion of carbon:

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

then

$$\Delta H_{rxn} = \Delta H_f\left[CO_2\left(g\right)\right]$$

The sign convention for ΔH_f is the same as for any enthalpy change: $\Delta H_f < 0$ if heat is released when elements combine to form a compound and $\Delta H_f > 0$ if heat is absorbed.

> The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

Standard Enthalpies of Formation

The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution), the pressure of any gases present, and the temperature at which the reaction is carried out. To avoid confusion caused by differences in reaction conditions and ensure uniformity of data, the scientific community has selected a specific set of conditions under which enthalpy changes are measured. These standard conditions serve as a reference point for measuring differences in enthalpy, much as sea level is the reference point for measuring the height of a mountain or for reporting the altitude of an airplane.

The standard conditions for which most thermochemical data are tabulated are a *pressure* of 1 atmosphere (atm) for all gases and a *concentration* of 1 M for all species in solution (1 mol/L). In addition, each pure substance must be in its standard state, which is usually its most stable form at a pressure of 1 atm at a specified temperature. We assume a temperature of 25°C (298 K) for all enthalpy changes given in this text, unless otherwise indicated. Enthalpies of formation measured under these conditions are called **standard enthalpies of formation** (ΔH_f^o) The enthalpy change for the formation of 1 mol of a compound from its component elements when the component elements are each in their standard states. The standard enthalpy of formation of any element in its most stable form is zero by definition.

> The standard enthalpy of formation of any element in its standard state is zero by definition.

For example, although oxygen can exist as ozone (O_3), atomic oxygen (O), and molecular oxygen (O_2), O_2 is the most stable form at 1 atm pressure and 25°C. Similarly, hydrogen is H_2(g), not atomic hydrogen (H). Graphite and diamond are both forms of elemental carbon, but because graphite is more stable at 1 atm pressure and 25°C, the standard state of carbon is graphite (Figure 1.9.1). Therefore, $\mathrm{O_2\,(g)}$, $\mathrm{H_2\,(g)}$, and graphite have ΔH_f^o values of zero.

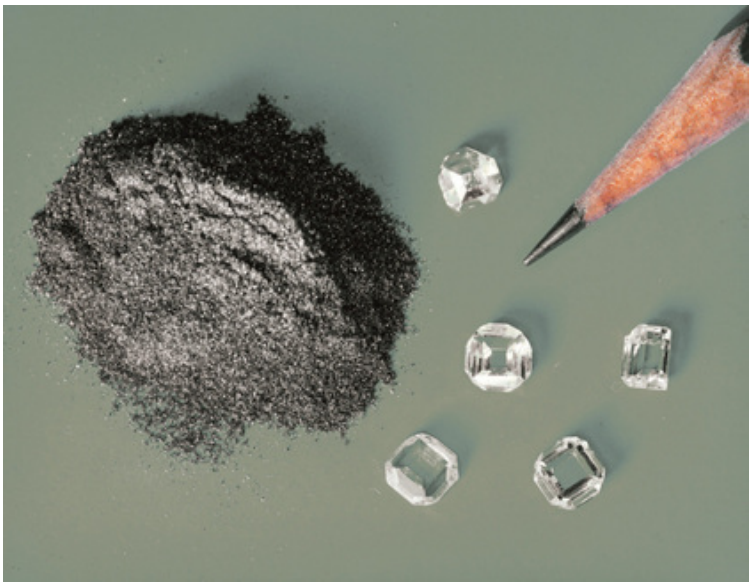


Figure 1.9.1: Elemental Carbon. Although graphite and diamond are both forms of elemental carbon, graphite is slightly more stable at 1 atm pressure and 25°C than diamond is. Given enough time, diamond will revert to graphite under these conditions. Hence graphite is the standard state of carbon.

The standard enthalpy of formation of glucose from the elements at 25°C is the enthalpy change for the following reaction:

[redacted]

It is not possible to measure the value of $\Delta H^o o_f$ for glucose, –1273.3 kJ/mol, by simply mixing appropriate amounts of graphite, $\mathrm{O_2}$, and $\mathrm{H_2}$ and measuring the heat evolved as glucose is formed since the reaction shown in Equation 1.9.905 does not occur at a measurable rate under any known conditions. Glucose is not unique; most compounds cannot be prepared by the chemical equations that define their standard enthalpies of formation. Instead, values of $\Delta H^o o_f$ are obtained using **Hess's law** and standard enthalpy changes that have been measured for other reactions, such as combustion reactions. Values of ΔH_f^o for an extensive list of compounds are given in Table T1. Note that ΔH_f^o values are always reported in kilojoules per mole of the substance of interest. Also notice in Table T1 that the standard enthalpy of formation of O_2(g) is zero because it is the most stable form of oxygen in its standard state.

Example 1.9.1: Enthalpy of Formation

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $\mathrm{HCl\,(g)}$
b. $\mathrm{MgCO_3\,(s)}$
c. $\mathrm{CH_3(CH_2)_{14}CO_2H\,(s)}$ (*palmitic acid*)

Given:

compound formula and phase.

Asked for:

balanced chemical equation for its formation from elements in standard states

Strategy:

Use Table T1 to identify the standard state for each element. Write a chemical equation that describes the formation of the compound from the elements in their standard states and then balance it so that 1 mol of product is made.

Solution:

To calculate the standard enthalpy of formation of a compound, we must start with the elements in their standard states. The standard state of an element can be identified in Table T1: by a ΔH_f^o value of 0 kJ/mol.

Hydrogen chloride contains one atom of hydrogen and one atom of chlorine. Because the standard states of elemental hydrogen and elemental chlorine are $\mathrm{H_2\,(g)}$ and $\mathrm{Cl_2\,(g)}$, respectively, the unbalanced chemical equation is

$$\mathrm{H_2\,(g) + Cl_2\,(g) \rightarrow HCl\,(g)}$$

Fractional coefficients are required in this case because ΔH^o_f values are reported for *1 mol* of the product, HCl. Multiplying both $\mathrm{H_2\,(g)}$ and $\mathrm{Cl_2\,(g)}$ by 1/2 balances the equation:

$$\mathrm{\tfrac{1}{2}\,H_2\,(g) + \tfrac{1}{2}\,Cl_2\,(g) \rightarrow HCl\,(g)}$$

The standard states of the elements in this compound are $\mathrm{Mg\,(s)}$, $\mathrm{C\,(s, graphite)}$, and $\mathrm{O_2\,(g)}$. The unbalanced chemical equation is thus

$$\mathrm{Mg\,(s) + C\,(s, graphite) + O_2\,(g) \rightarrow MgCO_3\,(s)}$$

This equation can be balanced by inspection to give

$$\mathrm{Mg\,(s) + C\,(s, graphite) + \tfrac{3}{2}\,O_2\ (g) \rightarrow MgCO_3\,(s)}$$

Palmitic acid, the major fat in meat and dairy products, contains hydrogen, carbon, and oxygen, so the unbalanced chemical equation for its formation from the elements in their standard states is as follows:

$$\mathrm{C\,(s, graphite) + H_2\,(g) + O_2\,(g) \rightarrow CH_3(CH_2)_{14}CO_2H\,(s)}$$

There are 16 carbon atoms and 32 hydrogen atoms in 1 mol of palmitic acid, so the balanced chemical equation is

$$\mathrm{16\,C\,(s, graphite) + 16\,H_2\,(g) + O_2\,(g) \longrightarrow CH_3(CH_2)_{14}CO_2H\,(s)}$$

Exercise 1.9.1

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $\mathrm{NaCl\,(s)}$
b. $\mathrm{H_2SO_4\,(l)}$

c. $\mathrm{CH_3CO_2H\,(l)}$ (*acetic acid*)

Answer a

$$\mathrm{Na\,(s) + \tfrac{1}{2}\,Cl_2\,(g) \;\rightarrow NaCl\,(s)}$$

Answer b

$$\mathrm{H_2\,(g) + \tfrac{1}{8}\,S_8\,(s) + 2\,O_2\;(\;g) \;\rightarrow H_2\;SO_4(\;l)}$$

Answer c

$$\mathrm{2\,C\,(s) + O_2\,(g) + 2\,H_2\,(g) \longrightarrow CH_3CO_2H\,(l)}$$

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https://www.youtube.com/embed/A20k0CK4doI?vq=hd1080

Definition of Heat of Formation Reactions: https://youtu.be/A20k0CK4doI

Standard Enthalpies of Reaction

Tabulated values of standard enthalpies of formation can be used to calculate enthalpy changes for *any* reaction involving substances whose ΔH_f^o values are known. The standard enthalpy of reaction ΔH_{rxn}^o is the enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard states. Consider the general reaction

[redacted]

where A, B, C, and D are chemical substances and a, b, c, and d are their stoichiometric coefficients. The magnitude of ΔH^o is the sum of the standard enthalpies of formation of the products, each multiplied by its appropriate coefficient, minus the sum of the standard enthalpies of formation of the reactants, also multiplied by their coefficients:

[redacted]

More generally, we can write

[redacted]

where the symbol $\sum$ means “sum of” and m and n are the stoichiometric coefficients of each of the products and the reactants, respectively. “Products minus reactants” summations such as Equation 1.9.908 arise from the fact that enthalpy is a state function. Because many other thermochemical quantities are also state functions, “products minus reactants” summations are very common in chemistry; we will encounter many others in subsequent chapters.

> "Products minus reactants" summations are typical of state functions.

To demonstrate the use of tabulated ΔH^{o} values, we will use them to calculate ΔH_{rxn} for the combustion of glucose, the reaction that provides energy for your brain:

[redacted]

Using Equation 1.9.908, we write

[redacted]

From Table T1, the relevant ΔH^{o}_{f} values are $\Delta H^{o}_{f}\,[CO_2(g)]$ = -393.5 kJ/mol, $\Delta H^{o}_{f}\,[H_2O(l)]$ = -285.8 kJ/mol, and $\Delta H^{o}_{f}\,[C_6H_{12}O_6(s)]$ = -1273.3 kJ/mol. Because $O_2(g)$ is a pure element in its standard state, $\Delta H^{o}_{f}\,[O_2(g)]$ = 0 kJ/mol. Inserting these values into Equation 1.9.910 and changing the subscript to indicate that this is a combustion reaction, we obtain

[redacted]

As illustrated in Figure 1.9.2, we can use Equation 1.9.911 to calculate ΔH^{o}_{f} for glucose because enthalpy is a state function. The figure shows two pathways from reactants (middle left) to products (bottom). The more direct pathway is the downward green arrow labeled ΔH^{o}_{comb}. The alternative hypothetical pathway consists of **four separate reactions** that convert the reactants to the elements in their standard states (upward purple arrow at left) and then convert the elements into the desired products (downward purple arrows at right). The reactions that convert the reactants to the elements are the reverse of the equations that define the ΔH^{o}_{f} values of the reactants. Consequently, the enthalpy changes are

[redacted]

> Recall that when we reverse a reaction, we must also reverse the **sign** of the accompanying enthalpy change (Equation 1.9.907 since the products are now reactants and vice versa.

The overall enthalpy change for conversion of the reactants (1 mol of glucose and 6 mol of O_2) to the elements is therefore +1273.3 kJ.

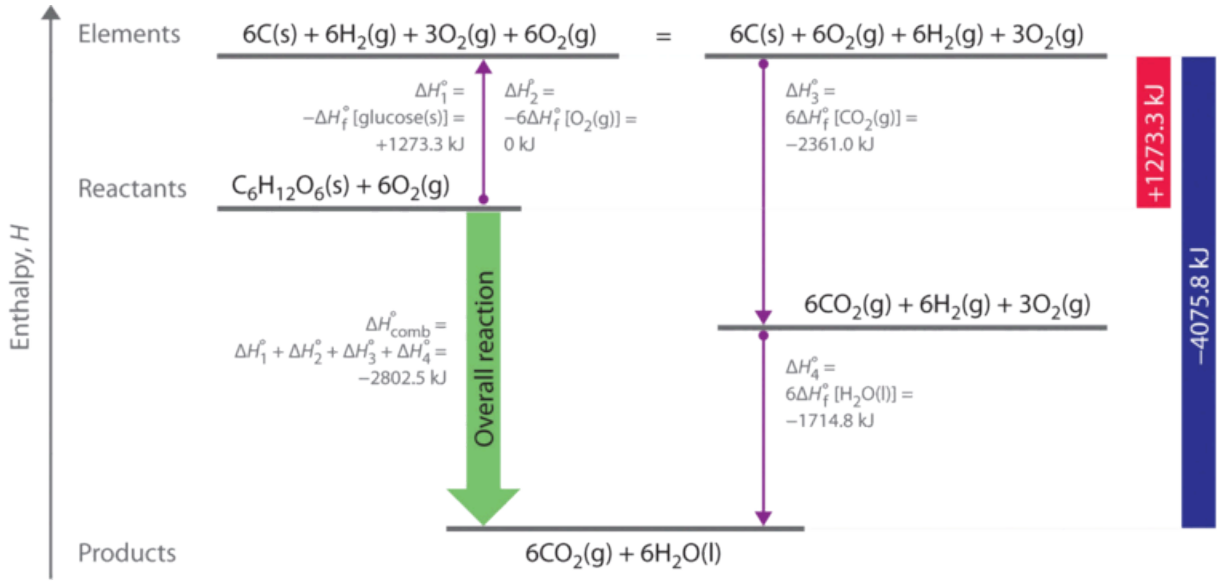


Figure 1.9.1: A Thermochemical Cycle for the Combustion of Glucose. Two hypothetical pathways are shown from the reactants to the products. The green arrow labeled ΔH^{o}_{comb} indicates the combustion reaction. Alternatively, we could first convert the reactants to the elements via the reverse of the equations that define their standard enthalpies of formation (the upward arrow, labeled ΔH^{o}_{1} and ΔH^{o}_{2}). Then we could convert the elements to the products via the equations used to define their standard enthalpies of formation (the downward arrows, labeled ΔH^{o}_{3} and ΔH^{o}_{4}). Because enthalpy is a state function, ΔH^{o}_{comb} is equal to the sum of the enthalpy changes $\Delta H^{o}_{1} + \Delta H^{o}_{2} + \Delta H^{o}_{3} + \Delta H^{o}_{4}$.

The reactions that convert the elements to final products (downward purple arrows in Figure 1.9.2) are identical to those used to define the ΔH^{o}_{f} values of the products. Consequently, the enthalpy changes (from Table T1) are

$$\Delta H^{o}_{3} = \Delta H^{o}_{f}\left[CO_2\left(g\right)\right] = 6\ \cancel{mol\ CO_2}\left(\frac{393.5\ kJ}{1\ \cancel{mol\ CO_2}}\right) = -2361.0\ kJ$$
$$\Delta H^{o}_{4} = 6\Delta H^{o}_{f}\left[H_2O\left(l\right)\right] = 6\ \cancel{mol\ H_2O}\left(\frac{-285.8\ kJ}{1\ \cancel{mol\ H_2O}}\right) = -1714.8\ kJ \tag{1.9.1415}$$

The overall enthalpy change for the conversion of the elements to products (6 mol of carbon dioxide and 6 mol of liquid water) is therefore –4075.8 kJ. Because enthalpy is a state function, the difference in enthalpy between an initial state and a final state can be computed using *any* pathway that connects the two. Thus the enthalpy change for the combustion of glucose to carbon dioxide and water is the sum of the enthalpy changes for the conversion of glucose and oxygen to the elements (+1273.3 kJ) and for the conversion of the elements to carbon dioxide and water (–4075.8 kJ):

[redacted]

This is the same result we obtained using the “products minus reactants” rule (Equation 1.9.908) and ΔH^{o}_{f} values. The two results must be the same because Equation 1.9.915 is just a more compact way of describing the thermochemical cycle shown in Figure 1.9.1.

Example 1.9.2: Heat of Combustion

Long-chain fatty acids such as palmitic acid ($CH_3(CH_2)_{14}CO_2H$) are one of the two major sources of energy in our diet (ΔH^{o}_{f} =–891.5 kJ/mol). Use the data in Table T1 to calculate ΔH^{o}_{comb} for the combustion of palmitic acid. Based on the energy released in combustion *per gram*, which is the better fuel — glucose or palmitic acid?

Given: compound and ΔH^{o}_{f} values

Asked for: ΔH^o_{comb} per mole and per gram

Strategy:

A. After writing the balanced chemical equation for the reaction, use Equation 1.9.908 and the values from Table T1 to calculate ΔH^o_{comb} the energy released by the combustion of 1 mol of palmitic acid.
B. Divide this value by the molar mass of palmitic acid to find the energy released from the combustion of 1 g of palmitic acid. Compare this value with the value calculated in Equation 1.9.911 for the combustion of glucose to determine which is the better fuel.

Solution:

A To determine the energy released by the combustion of palmitic acid, we need to calculate its ΔH^o_f. As always, the first requirement is a balanced chemical equation:

$$C_{16}H_{32}O_{2(s)} + 23O_{2(g)} \rightarrow 16CO_{2(g)} + 16H_2O_{(l)}$$

Using Equation 1.9.908 ("products minus reactants") with ΔH^0_f values from Table T1 (and omitting the physical states of the reactants and products to save space) gives

$$\begin{aligned}\Delta H^o_{comb} &= \sum m\Delta H^o_f\,(products) - \sum n\Delta H^o_f\,(reactants)\\ &= [16\,(-393.5\ kJ/mol\ CO_2) + 16\,(-285.8\ kJ/mol\ H_2O\ )]\\ &\quad - [-891.5\ kJ/mol\ C_{16}H_{32}O_2 + 23\,(0\ kJ/mol\ O_2\ )]\\ &= -9977.3\ kJ/mol\end{aligned}$$

This is the energy released by the combustion of 1 mol of palmitic acid.

B The energy released by the combustion of 1 g of palmitic acid is

$$\Delta H^o_{comb}\ \ per\ \ gram = \left(\frac{9977.3\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{256.42\ g}\right) = -38.910\ \ kJ/g$$

As calculated in Equation 1.9.911, \(ΔH^o_f\) of glucose is –2802.5 kJ/mol. The energy released by the combustion of 1 g of glucose is therefore

$$\Delta H^o_{comb}\ \ per\ \ gram = \left(\frac{-2802.5\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{180.16\ g}\right) = -15.556\ \ kJ/g$$

The combustion of fats such as palmitic acid releases more than twice as much energy per gram as the combustion of sugars such as glucose. This is one reason many people try to minimize the fat content in their diets to lose weight.

Exercise 1.9.2: Water–gas shift reaction

Use Table T1 to calculate ΔH^o_{rxn} for the *water–gas shift reaction*, which is used industrially on an enormous scale to obtain H_2(g):

$$\mathrm{CO\ (\ g\ ) + H_2O\ (g\ ) \longrightarrow CO_2\,(g) + H_2\ (\ g\ )}$$

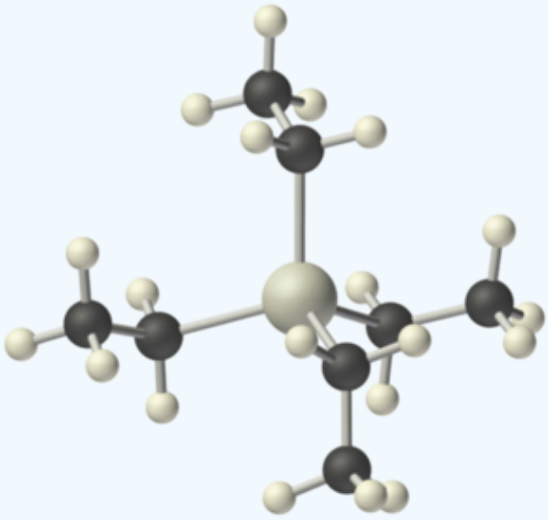
Answer

−41.2 kJ/mol

We can also measure the enthalpy change for another reaction, such as a combustion reaction, and then use it to calculate a compound's ΔH_f^o which we cannot obtain otherwise. This procedure is illustrated in Example 1.9.3.

Example 1.9.3: Tetraethyllead

Beginning in 1923, tetraethyllead [$(C_2H_5)_4Pb$] was used as an antiknock additive in gasoline in the United States. Its use was completely phased out in 1986 because of the health risks associated with chronic lead exposure. Tetraethyllead is a highly poisonous, colorless liquid that burns in air to give an orange flame with a green halo. The combustion products are $CO_2\,(g)$, $H_2O\,(l)$, and red $PbO\,(s)$. What is the standard enthalpy of formation of tetraethyllead, given that ΔH_f^o is −19.29 kJ/g for the combustion of tetraethyllead and ΔH_f^o of red PbO(s) is −219.0 kJ/mol?



Tetraethyllead

Given: reactant, products, and ΔH_{comb}^o values

Asked for: ΔH_f^o of the reactants

Strategy:

A. Write the balanced chemical equation for the combustion of tetraethyl lead. Then insert the appropriate quantities into Equation 1.9.908 to get the equation for ΔH^0_f of tetraethyl lead.
B. Convert ΔH_{comb}^o per gram given in the problem to ΔH_{comb}^o per mole by multiplying ΔH_{comb}^o per gram by the molar mass of tetraethyllead.
C. Use Table T1 to obtain values of ΔH_f^o for the other reactants and products. Insert these values into the equation for ΔH_f^o of tetraethyl lead and solve the equation.

Solution:

A The balanced chemical equation for the combustion reaction is as follows:

$$2\,(C_2H_5)_4Pb\,(l) + 27\,O_2\,(g) \longrightarrow 2\,PbO\,(s) + 16\,CO_2\,(g) + 20\,H_2O\,(l)$$

Using Equation 1.9.908 gives

$$\Delta H^o_{comb} = \left[2\Delta H^o_f\,(PbO) + 16\Delta H^o_f\,(CO_2) + 20\Delta H^o_f\,(H_2O)\right] - \left[2\Delta H^o_f\,((C_2H_5)_4\,Pb) + 27\Delta H^o_f\,(O_2)\right]$$

Solving for $\Delta H^o_f[(C_2H_5)_4Pb]$ gives

$$\Delta H^o_f\,((C_2H_5)_4\,Pb) = \Delta H^o_f\,(PbO) + 8\Delta H^o_f\,(CO_2) + 10\Delta H^o_f\,(H_2O) - \frac{27}{2}\Delta H^o_f\,(O_2) - \frac{\Delta H^o_{comb}}{2}$$

The values of all terms other than $\Delta H^o_f[(C_2H_5)_4Pb]$ are given in Table T1.

B The magnitude of ΔH^o_{comb} is given in the problem in kilojoules per *gram* of tetraethyl lead. We must therefore multiply this value by the molar mass of tetraethyl lead (323.44 g/mol) to get ΔH^o_{comb} for 1 mol of tetraethyl lead:

$$\Delta H^o_{comb} = \left(\frac{-19.29\ kJ}{\cancel{g}}\right)\left(\frac{323.44\ \cancel{g}}{mol}\right)$$
$$= -6329\ kJ/mol$$

Because the balanced chemical equation contains 2 mol of tetraethyllead, ΔH^o_{rxn} is

$$\Delta H^o_{rxn} = 2\ \cancel{mol\ (C_2H5)_4\,Pb}\left(\frac{-6329\ kJ}{1\ \cancel{mol\ (C_2H5)_4\,Pb}}\right)$$
$$= -12,480\ kJ$$

C Inserting the appropriate values into the equation for $\Delta H^o_f[(C_2H_5)_4Pb]$ gives

$$\Delta H^o_f\,[(C_2H_4)_4\,Pb] = [1\ mol\ PbO\ \times 219.0\ kJ/mol] + [8\ mol\ CO_2 \times (-393.5\ kJ/mol)] + [10\ mol\ H_2O \times (-285.8\ kJ/mol)] + [-27/2\ mol\ O_2) \times 0\ kJ/mol\ O_2]\,[12,480.2\ kJ/mol\ \ (C_2H_5)_4\,Pb]$$
$$= -219.0\ kJ - 3148\ kJ - 2858kJ - 0kJ + 6240\ kJ = 15kJ/mol$$

Exercise 1.9.3

Ammonium sulfate, $(NH_4)_2SO_4$, is used as a fire retardant and wood preservative; it is prepared industrially by the highly exothermic reaction of gaseous ammonia with sulfuric acid:

$$2\,NH_3\,(g) + H_2SO_4\,(aq)\ \rightarrow (NH_4)_2SO_4\,(s)$$

The value of ΔH^o_{rxn} is -179.4 kJ/mole H_2SO_4. Use the data in Table T1 to calculate the standard enthalpy of formation of ammonium sulfate (in kilojoules per mole).

Answer

–1181 kJ/mol

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online
https://www.youtube.com/embed/Y3aJJno9W2c?vq=hd1080

Calculating DH° using DHf°: https://youtu.be/Y3aJJno9W2c

Summary

- The standard state for measuring and reporting enthalpies of formation or reaction is 25 ^{o}C and 1 atm.
- The elemental form of each atom is that with the lowest enthalpy in the standard state.
- The standard state heat of formation for the elemental form of each atom is zero.

The **enthalpy of formation** (ΔH_f) is the enthalpy change that accompanies the formation of a compound from its elements. **Standard enthalpies of formation** (ΔH_f^o) are determined under **standard conditions**: a pressure of 1 atm for gases and a concentration of 1 M for species in solution, with all pure substances present in their **standard states** (their most stable forms at 1 atm pressure and the temperature of the measurement). The standard heat of formation of any element in its most stable form is defined to be zero. The **standard enthalpy of reaction** (ΔH_{rxn}^o) can be calculated from the sum of the **standard enthalpies of formation** of the products (each multiplied by its stoichiometric coefficient) minus the sum of the standard enthalpies of formation of the reactants (each multiplied by its stoichiometric coefficient)—the “products minus reactants” rule. The **enthalpy of solution** (ΔH_{soln}) is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

Contributors and Attributions

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1.10: Fuels as Sources of Energy

Learning Objectives

- To use thermochemical concepts to solve environmental issues.

Our contemporary society requires the constant expenditure of huge amounts of energy to heat our homes, provide telephone and cable service, transport us from one location to another, provide light when it is dark outside, and run the machinery that manufactures material goods. The United States alone consumes almost 10^6 kJ per person per day, which is about 100 times the normal required energy content of the human diet. This figure is about 30% of the world's total energy usage, although only about 5% of the total population of the world lives in the United States. In contrast, the average energy consumption elsewhere in the world is about 10^5 kJ per person per day, although actual values vary widely depending on a country's level of industrialization. In this section, we describe various sources of energy and their impact on the environment.

Fuels

According to the law of conservation of energy, energy can never actually be "consumed"; it can only be changed from one form to another. What *is* consumed on a huge scale, however, are resources that can be readily converted to a form of energy that is useful for doing work. Energy that is not used to perform work is either stored as potential energy for future use or transferred to the surroundings as heat.

A major reason for the huge consumption of energy by our society is the low *efficiency* of most machines in transforming stored energy into work. Efficiency can be defined as the ratio of useful work accomplished to energy expended. Automobiles, for example, are only about 20% efficient in converting the energy stored in gasoline to mechanical work; the rest of the energy is released as heat, either emitted in the exhaust or produced by friction in bearings and tires. The production of electricity by coal- or oil-powered steam turbines (Figure 1.10.1) is can be more than 50% efficient.

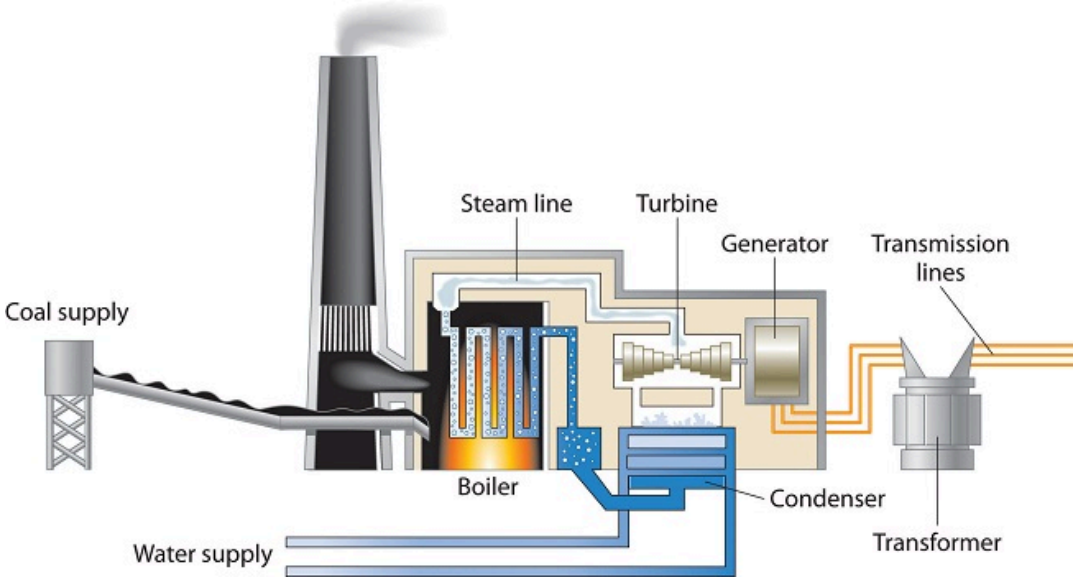


Figure 1.10.1: Electricity from Coal. A coal-powered electric power plant uses the combustion of coal to produce steam, which drives a turbine to produce electricity.

In general, it is more efficient to use primary sources of energy directly (such as natural gas or oil) than to transform them to a secondary source such as electricity prior to their use. For example, if a furnace is well maintained, heating a house with natural gas is about 70% efficient. In contrast, burning the natural gas in a remote power plant, converting it to electricity, transmitting it long distances through wires, and heating the house by electric baseboard heaters have an overall efficiency of less than 35%.

The total expenditure of energy in the world each year is about 3×10^{17} kJ. 80% of this energy is provided by the combustion of fossil fuels: oil, coal, and natural gas (the sources of the energy consumed in the United States in 2019 are shown in Figure 1.10.2). Natural gas and petroleum are the preferred fuels because many of the products derived from them are gases or liquids that are readily transported, stored, and burned. Natural gas and petroleum are derived from the remains of marine creatures that died hundreds of millions of years ago and were buried beneath layers of sediment. As the sediment turned to rock, the tremendous heat and pressure inside Earth transformed the organic components of the buried sea creatures to petroleum and natural gas.

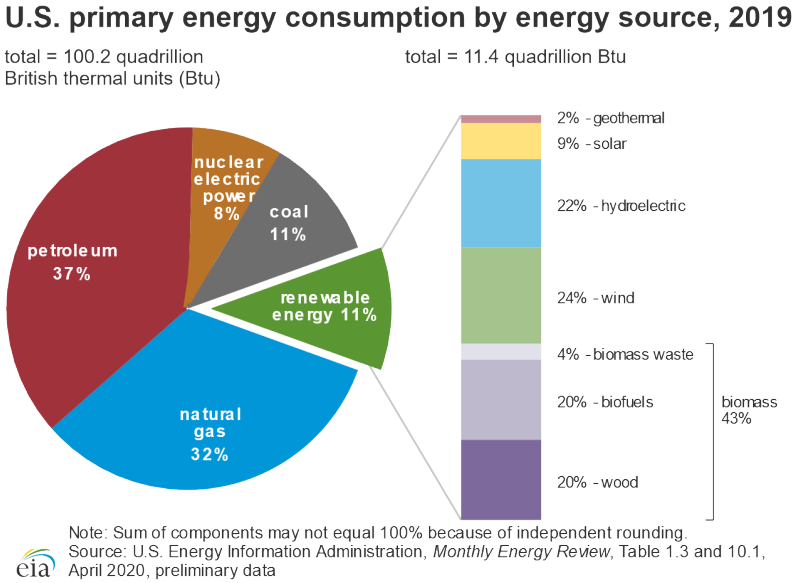


Figure 1.10.2: Energy Consumption in the United States by Source, 2014. More than 75% of the total energy expended is provided by the combustion of fossil fuels, such as oil, coal, and natural gas. (Public Domain; U.S. Energy Information Administration)

Coal

Coal is a complex solid material derived primarily from plants that died and were buried hundreds of millions of years ago and were subsequently subjected to high temperatures and pressures. Because plants contain large amounts of *cellulose*, derived from linked glucose units, the structure of coal is more complex than that of petroleum (Figure 1.10.3). In particular, coal contains a large number of oxygen atoms that link parts of the structure together, in addition to the basic framework of carbon–carbon bonds. It is impossible to draw a single structure for coal; however, because of the prevalence of rings of carbon atoms (due to the original high cellulose content), coal is more similar to an aromatic hydrocarbon than an aliphatic one.

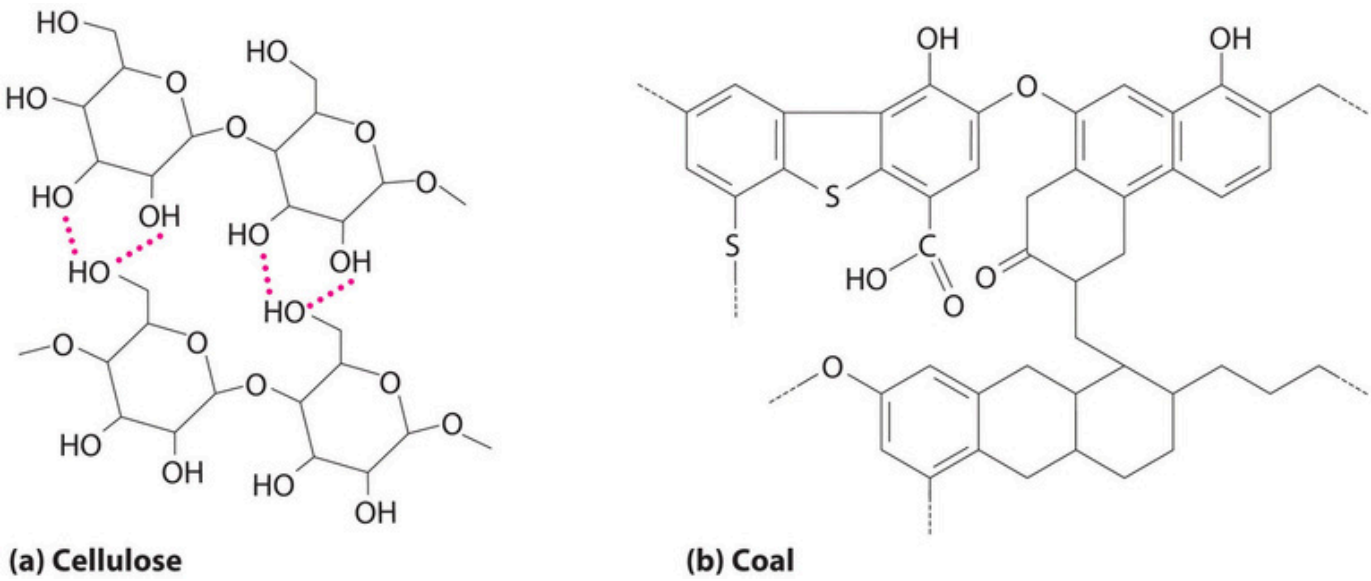


Figure 1.10.3: The Structures of Cellulose and Coal. (a) Cellulose consists of long chains of cyclic glucose molecules linked by hydrogen bonds. (b) When cellulose is subjected to high pressures and temperatures for long periods of time, water is eliminated, and bonds are formed between the rings, eventually producing coal. This drawing shows some of the common structural features of coal; note the presence of many different kinds of ring structures.

Table 1.10.1: Properties of Different Types of Coal

Type	% Carbon	Hydrogen:Carbon Mole Ratio	% Oxygen	% Sulfur	Heat Content	US Deposits
anthracite	92	0.5	3	1	high	Pennsylvania, New York
bituminous	80	0.6	8	5	medium	Appalachia, Midwest, Utah
subbituminous	77	0.9	16	1	medium	Rocky Mountains
lignite	71	1.0	23	1	low	Montana

There are four distinct classes of coal (Table 1.10.1); their hydrogen and oxygen contents depend on the length of time the coal has been buried and the pressures and temperatures to which it has been subjected. Lignite, with a hydrogen:carbon ratio of about 1.0 and a high oxygen content, has the lowest ΔH_{comb}. Anthracite, in contrast, with a hydrogen:carbon ratio of about 0.5 and the lowest oxygen content, has the highest ΔH_{comb} and is the highest grade of coal. The most abundant form in the United States is bituminous coal, which has a high sulfur content because of the presence of small particles of pyrite (FeS_2). The combustion of coal releases the sulfur in FeS_2 as SO_2, which is a major contributor to acid rain. Table 1.10.2 compares the ΔH_{comb} per gram of oil, natural gas, and coal with those of selected organic compounds.

Table 1.10.2: Enthalpies of Combustion of Common Fuels and Selected Organic Compounds

Fuel	ΔH_{comb} (kJ/g)
dry wood	−15
peat	−20.8
bituminous coal	−28.3
charcoal	−35
kerosene	−37
C_6H_6 (benzene)	−41.8
crude oil	−43
natural gas	−50
C_2H_2 (acetylene)	−50.0

Fuel	ΔH_{comb} (kJ/g)
CH_4 (methane)	–55.5
gasoline	–84
hydrogen	–143

Peat, a precursor to coal, is the partially decayed remains of plants that grow in swampy areas. It is removed from the ground in the form of soggy bricks of mud that will not burn until they have been dried. Even though peat is a smoky, poor-burning fuel that gives off relatively little heat, humans have burned it since ancient times (Figure 1.10.4). If a peat bog were buried under many layers of sediment for a few million years, the peat could eventually be compressed and heated enough to become lignite, the lowest grade of coal; given enough time and heat, lignite would eventually become anthracite, a much better fuel.



Figure 1.10.4: A Peat Bog. Peat is a smoky fuel that burns poorly and produces little heat, but it has been used as a fuel since ancient times.

Converting Coal to Gaseous and Liquid Fuels

Oil and natural gas resources are limited. Current estimates suggest that the known reserves of petroleum will be exhausted in about 60 years, and supplies of natural gas are estimated to run out in about 120 years. Coal, on the other hand, is relatively abundant, making up more than 90% of the world's fossil fuel reserves. As a solid, coal is much more difficult to mine and ship than petroleum (a liquid) or natural gas. Consequently, more than 75% of the coal produced each year is simply burned in power plants to produce electricity. A great deal of current research focuses on developing methods to convert coal to gaseous fuels (*coal* gasification) or liquid fuels (coal liquefaction). In the most common approach to coal gasification, coal reacts with steam to produce a mixture of CO and H2 known as synthesis gas, or syngas:Because coal is 70%–90% carbon by mass, it is approximated as C in Equation 1.10.916.

[redacted]

Converting coal to syngas removes any sulfur present and produces a clean-burning mixture of gases.

Syngas is also used as a reactant to produce methane and methanol. A promising approach is to convert coal directly to methane through a series of reactions:

[redacted]

Burning a small amount of coal or methane provides the energy consumed by these reactions. Unfortunately, methane produced by this process is currently significantly more expensive than natural gas. As supplies of natural gas become depleted, however, this coal-based process may well become competitive in cost.



Measuring crude oil. The standard industrial unit of measure for crude oil is the 42 gal barrel.

Similarly, the techniques available for converting coal to liquid fuels are not yet economically competitive with the production of liquid fuels from petroleum. Current approaches to coal liquefaction use a catalyst to break the complex network structure of coal into more manageable fragments. The products are then treated with hydrogen (from syngas or other sources) under high pressure to produce a liquid more like petroleum. Subsequent distillation, cracking, and reforming can be used to create products similar to those obtained from petroleum. The total yield of liquid fuels is about 5.5 bbl of crude liquid per ton of coal (1 bbl is 42 gal or 160 L). Although the economics of coal liquefaction are currently even less attractive than for coal gasification, liquid fuels based on coal are likely to become economically competitive as supplies of petroleum are consumed.

Example 1.10.1

If bituminous coal is converted to methane by the process in Equation 1.10.916, what is the ratio of the ΔH_{comb} of the methane produced to the enthalpy of the coal consumed to produce the methane? (Note that 1 mol of CH_4 is produced for every 2 mol of carbon in coal.)

Given: chemical reaction and ΔH_{comb} (Table 1.10.2)

Asked for: ratio of ΔH_{comb} of methane produced to coal consumed

Strategy:

A Write a balanced chemical equation for the conversion of coal to methane. Referring to Table 1.10.2, calculate the ΔH_{comb} of methane and carbon.

B Calculate the ratio of the energy released by combustion of the methane to the energy released by combustion of the carbon.

Solution:

A The balanced chemical equation for the conversion of coal to methane is as follows:

$$2\,\mathrm{C}\,(\mathrm{s}) + 2\,\mathrm{H_2O}\,(\mathrm{g}) \longrightarrow \mathrm{CH_4}\,(\mathrm{g}) + \mathrm{CO_2}\,(\mathrm{g})$$

Thus 1 mol of methane is produced for every 2 mol of carbon consumed. The ΔH_{comb} of 1 mol of methane is

$$1\ \text{mol}\ \cancel{\text{CH}_4}\left(\frac{16.043\ \cancel{\text{g}}}{1\ \text{mol}\ \cancel{\text{CH}_4}}\right)\left(\frac{-55.5\ \text{kJ}}{\cancel{\text{g}}}\right) = -890\ \text{kJ}$$

The ΔH_{comb} of 2 mol of carbon (as coal) is

$$2\ \cancel{\text{mol C}}\left(\frac{12.011\ \cancel{\text{g}}}{1\ \cancel{\text{mol C}}}\right)\left(\frac{-28.3\ \text{kJ}}{\cancel{\text{g}}}\right) = -680\ \text{kJ}$$

B The ratio of the energy released from the combustion of methane to the energy released from the combustion of carbon is

$$\frac{-890\ \cancel{\text{kJ}}}{-680\ \cancel{\text{kJ}}} = 1.31$$

The energy released from the combustion of the product (methane) is 131% of that of the reactant (coal). The fuel value of coal is actually increased by the process!

How is this possible when the law of conservation of energy states that energy cannot be created? The reaction consumes 2 mol of water ($\Delta H_f^\circ = -285.8\ \text{kJ/mol}$) but produces only 1 mol of CO2 ($\Delta H_f^\circ = -393.5\ \text{kJ/mol}$). Part of the difference in potential energy between the two (approximately 180 kJ/mol) is stored in CH4 and can be released during combustion.

Exercise 1.10.1

Using the data in Table 1.10.2, calculate the mass of hydrogen necessary to provide as much energy during combustion as 1 bbl of crude oil (density approximately 0.75 g/mL).

Answer

36 kg

The Carbon Cycle and the Greenhouse Effect

Even if carbon-based fuels could be burned with 100% efficiency, producing only CO_2(g) and H_2O(g), doing so could still potentially damage the environment when carried out on the vast scale required by an industrial society. The amount of CO_2 released is so large and is increasing so rapidly that it is apparently overwhelming the natural ability of the planet to remove CO_2 from the atmosphere. In turn, the elevated levels of CO_2 are thought to be affecting the temperature of the planet through a mechanism known as the greenhouse effect. As you will see, there is little doubt that atmospheric CO_2 levels are increasing, and the major reason for this increase is the combustion of fossil fuels. There is substantially less agreement, however, on whether the increased CO_2 levels are responsible for a significant increase in temperature.

The Global Carbon Cycle

Figure 1.10.5 illustrates the global carbon cycle, the distribution and flow of carbon on Earth. Normally, the fate of atmospheric CO_2 is to either (1) dissolve in the oceans and eventually precipitate as carbonate rocks or (2) be taken up by plants. The rate of uptake of CO_2 by the ocean is limited by its surface area and the rate at which gases dissolve, which are approximately constant. The rate of uptake of CO_2 by plants, representing about 60 billion metric tons of carbon per year, partly depends on how much of Earth's surface is covered by vegetation. Unfortunately, the rapid deforestation for agriculture is reducing the overall amount of vegetation, and about 60 billion metric tons of carbon are released annually as CO_2 from animal respiration and plant decay. The amount of carbon released as CO_2 every year by fossil fuel combustion is estimated to be about 5.5 billion metric tons. The net result is a system that is slightly out of balance, experiencing a slow but steady increase in atmospheric CO_2 levels (Figure 1.10.6

). As a result, average CO_2 levels have increased by about 30% since 1850.

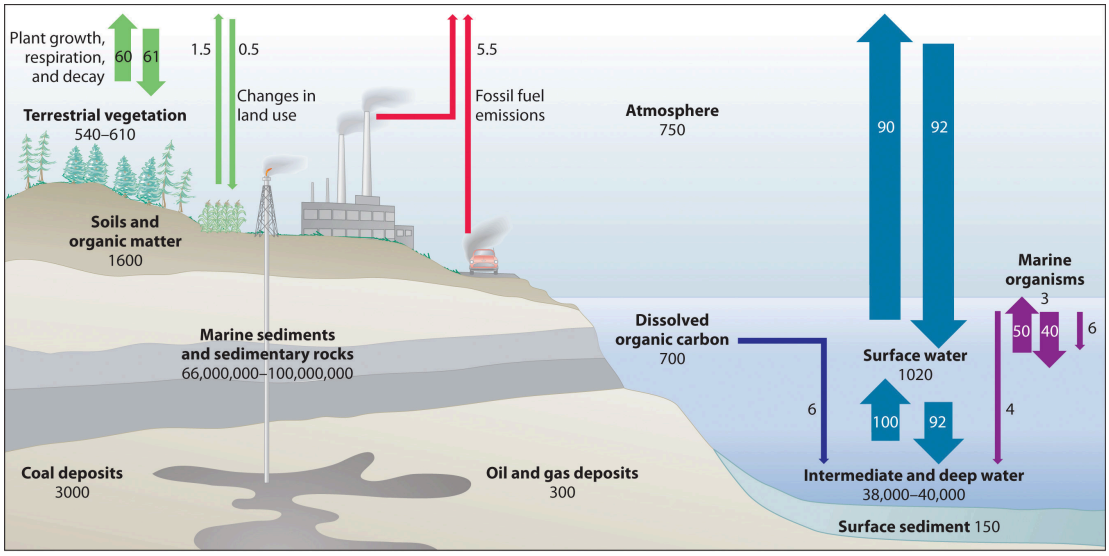
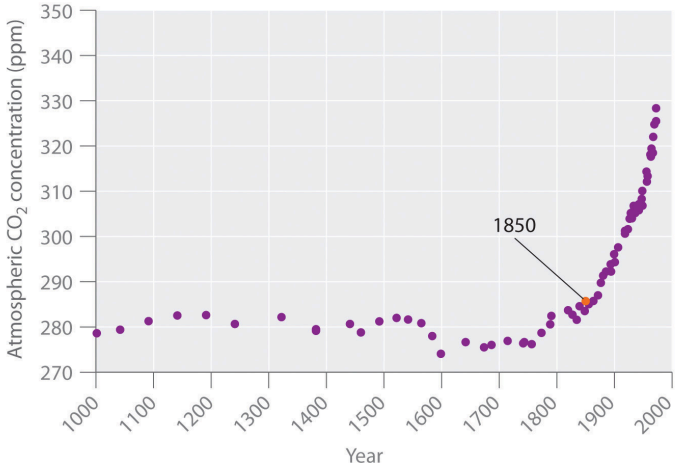
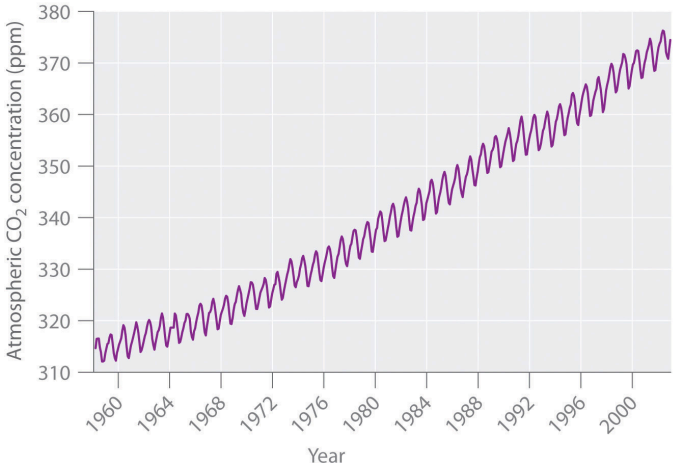


Figure 1.10.5: The Global Carbon Cycle

Most of Earth's carbon is found in the crust, where it is stored as calcium and magnesium carbonate in sedimentary rocks. The oceans also contain a large reservoir of carbon, primarily as the bicarbonate ion (HCO_3^-). Green plants consume about 60 billion metric tons of carbon per year as CO_2 during photosynthesis, and about the same amount of carbon is released as CO_2 annually from animal and plant respiration and decay. The combustion of fossil fuels releases about 5.5 billion metric tons of carbon per year as CO_2.



(a) Records from Antarctic ice cores (1006–1969)



(b) Records from monthly air samples, Mauna Loa Observatory, Hawaii (1958–2002)

Figure 1.10.6: Changes in Atmospheric CO_2 Levels. (a) Average worldwide CO_2 levels have increased by about 30% since 1850. (b) Atmospheric CO_2 concentrations measured at Mauna Loa in Hawaii show seasonal variations caused by the removal of CO_2 from the atmosphere by green plants during the growing season along with a general increase in CO_2 levels.

The Atmospheric Greenhouse Effect

The increasing levels of atmospheric CO_2 are of concern because CO_2 absorbs thermal energy radiated by the Earth, as do other gases such as water vapor, methane, and chlorofluorocarbons. Collectively, these substances are called greenhouse gases; they mimic the effect of a greenhouse by trapping thermal energy in the Earth's atmosphere, a phenomenon known as the greenhouse

effect (Figure 1.10.7).

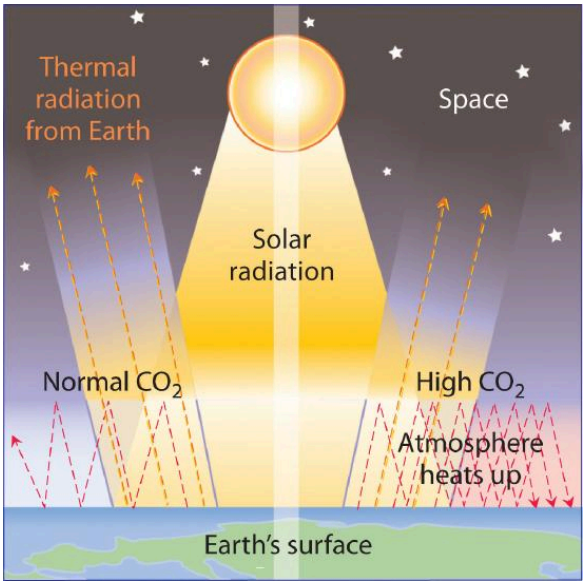


Figure 1.10.7: The Greenhouse Effect. Thermal energy can be trapped in Earth's atmosphere by gases such as CO_2, water vapor, methane, and chlorofluorocarbons before it can be radiated into space—like the effect of a greenhouse. It is not yet clear how large an increase in the temperature of Earth's surface can be attributed to this phenomenon.

Venus is an example of a planet that has a runaway greenhouse effect. The atmosphere of Venus is about 95 times denser than that of Earth and contains about 95% CO_2. Because Venus is closer to the sun, it also receives more solar radiation than Earth does. The result of increased solar radiation and high CO_2 levels is an average surface temperature of about 450°C, which is hot enough to melt lead.

Data such as those in Figure Figure 1.10.6 indicate that atmospheric levels of greenhouse gases have increased dramatically over the past 100 years, and it seems clear that the heavy use of fossil fuels by industry is largely responsible. It is not clear, however, how large an increase in temperature (*global warming*) may result from a continued increase in the levels of these gases. Estimates of the effects of doubling the preindustrial levels of CO_2 range from a 0°C to a 4.5°C increase in the average temperature of Earth's surface, which is currently about 14.4°C. Even small increases, however, could cause major perturbations in our planet's delicately balanced systems. For example, an increase of 5°C in Earth's average surface temperature could cause extensive melting of glaciers and the Antarctic ice cap. It has been suggested that the resulting rise in sea levels could flood highly populated coastal areas, such as New York City, Calcutta, Tokyo, Rio de Janeiro, and Sydney. An analysis conducted in 2009 by leading climate researchers from the US National Oceanic and Atmospheric Administration, Switzerland, and France shows that CO_2 in the atmosphere will remain near peak levels far longer than other greenhouse gases, which dissipate more quickly. The study predicts a rise in sea levels of approximately 3 ft by the year 3000, excluding the rise from melting glaciers and polar ice caps. According to the analysis, southwestern North America, the Mediterranean, and southern Africa are projected to face droughts comparable to that of the Dust Bowl of the 1930s as a result of global climate changes.

The increase in CO_2 levels is only one of many trends that can affect Earth's temperature. In fact, geologic evidence shows that the average temperature of Earth has fluctuated significantly over the past 400,000 years, with a series of glacial periods (during which the temperature was 10°C–15°C *lower* than it is now and large glaciers covered much of the globe) interspersed with relatively short, warm interglacial periods (Figure 1.10.8). Although average temperatures appear to have increased by 0.5°C in the last century, the statistical significance of this increase is open to question, as is the existence of a cause-and-effect relationship between the temperature change and CO_2 levels. Despite the lack of incontrovertible scientific evidence, however, many people believe that we should take steps now to limit CO_2 emissions and explore alternative sources of energy, such as solar energy, geothermal energy from volcanic steam, and nuclear energy, to avoid even the possibility of creating major perturbations in Earth's environment. In 2010, international delegates met in Cancún, Mexico, and agreed on a broad array of measures that would advance climate protection. These included the development of low-carbon technologies, providing a framework to reduce deforestation, and aiding countries in assessing their own vulnerabilities. They avoided, however, contentious issues of assigning emissions reductions commitments.

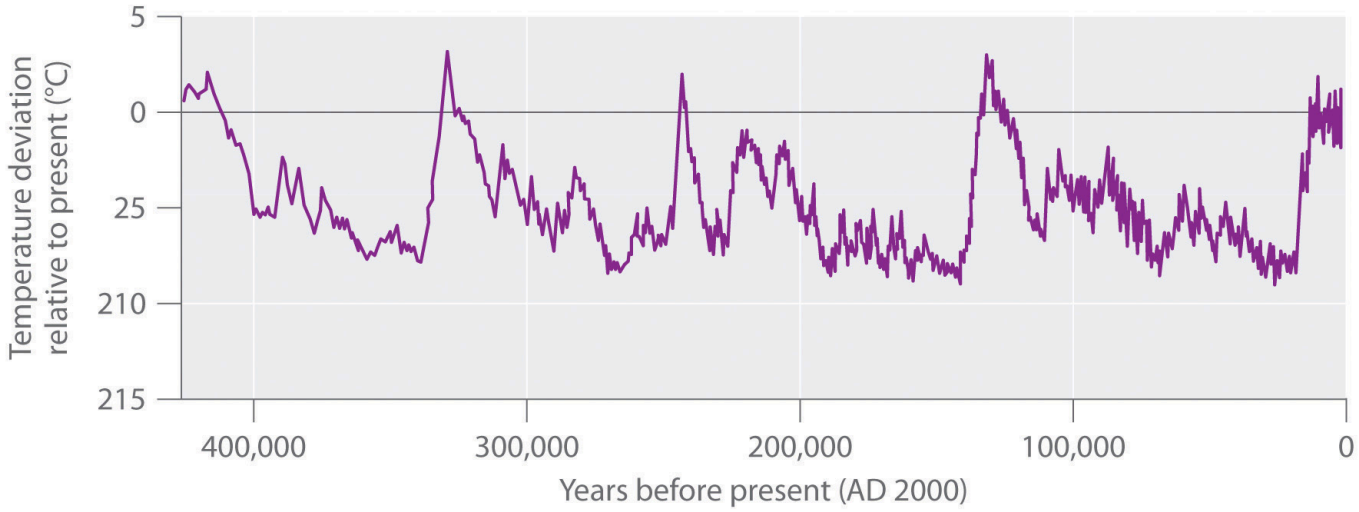


Figure 1.10.8: Average Surface Temperature of Earth over the Past 400,000 Years. The dips correspond to glacial periods, and the peaks correspond to relatively short, warm interglacial periods. Because of these fluctuations, the statistical significance of the 0.5°C increase in average temperatures observed in the last century is open to question.

Example 1.10.2

A student at UCLA decided to fly home to New York for Christmas. The round trip was 4500 air miles, and part of the cost of her ticket went to buy the 100 gal of jet fuel necessary to transport her and her baggage. Assuming that jet fuel is primarily *n*-dodecane ($C_{12}H_{26}$) with a density of 0.75 g/mL, how much energy was expended and how many tons of CO_2 were emitted into the upper atmosphere to get her home and back?

Given: volume and density of reactant in combustion reaction

Asked for: energy expended and mass of CO_2 emitted

Strategy:

A After writing a balanced chemical equation for the reaction, calculate $\Delta H^\circ_{\text{comb}}$

B Determine the number of moles of dodecane in 100 gal by using the density and molar mass of dodecane and the appropriate conversion factors.

C Obtain the amount of energy expended by multiplying $\Delta H^\circ_{\text{comb}}$ by the number of moles of dodecane. Calculate the amount of CO2 emitted in tons by using mole ratios from the balanced chemical equation and the appropriate conversion factors.

Solution

A We first need to write a balanced chemical equation for the reaction:

$$2\,C_{12}H_{26}\,(l) + 37\,O_2\,(g) \longrightarrow 24\,CO_2\,(g) + 26\,H_2O\,(l)$$

We can calculate $\Delta H^\circ_{\text{comb}}$ using the ΔH°_f values corresponding to each substance in the specified phase (phases are not shown for simplicity):

$$\begin{aligned}\Delta H^\circ_{\text{comb}} &= \Sigma m\Delta H^\circ_f(\text{products}) - \Sigma n\Delta H^\circ_f(\text{reactants})\\ &= [24\Delta H^\circ_f(CO_2) + 26\Delta H^\circ_f(H_2O)] - [37\Delta H^\circ_f(O_2) + 2\Delta H^\circ_f(C_{12}H_{26})]\\ &= [24(-393.5\ \text{kJ/mol } CO_2) + 26(-285.8\ \text{kJ/mol } H_2O)]\\ &\quad -[37(0\ \text{kJ/mol } O_2) + 2(-350.9\ \text{kJ/mol } C_{12}H_{26})]\\ &= -16,173.0\ \text{kJ}\end{aligned}$$

According to the balanced chemical equation for the reaction, this value is $\Delta H^\circ_{\text{comb}}$ for the combustion of 2 mol of n-dodecane. So we must divide by 2 to obtain $\Delta H^\circ_{\text{comb}}$ per mole of n-dodecane:

$$\Delta H^\circ_{\text{comb}} = -8,086.5\ \text{kJ/mol } C_{12}H_{26}$$

B The number of moles of dodecane in 100 gal can be calculated as follows, using density, molar mass, and appropriate conversion factors:

$$100\ \cancel{\text{gal}}\left(\frac{3.785\ \cancel{L}}{1\ \cancel{\text{gal}}}\right)\left(\frac{1000\ \cancel{\text{mL}}}{\cancel{L}}\right)\left(\frac{0.75\ \cancel{g}}{\cancel{\text{mL}}}\right)\left(\frac{1\ \text{mol}}{170.34\ \cancel{g}}\right) = 1.7\times10^3\ \text{mol } C_{12}H_{26}$$

C The total energy released is

$$\Delta H^\circ_{\text{comb}} = (-8086.5\ \text{kJ/}\cancel{\text{mol}})(1.7\times10^3\ \cancel{\text{mol}}) = -1.4\times10^7\ \text{kJ}$$

From the balanced chemical equation for the reaction, we see that each mole of dodecane forms 12 mol of CO_2 upon combustion. Hence the amount of CO_2 emitted is

$$1.7\times10^3\ \cancel{\text{mol } C_{12}H_{26}}\left(\frac{\frac{24}{2}\ \cancel{\text{mol } CO_2}}{1\ \cancel{\text{mol } C_{12}H_{26}}}\right)\left(\frac{44.0\ \cancel{g}}{1\ \cancel{\text{mol } CO_2}}\right)\left(\frac{1\ \cancel{\text{lb}}}{454\ \cancel{g}}\right)\left(\frac{1\ \text{tn}}{2000\ \cancel{\text{lb}}}\right) = 0.99\ \text{tn}$$

Exercise 1.10.2

Suppose the student in Example 1.10.2 couldn't afford the plane fare, so she decided to drive home instead. Assume that the round-trip distance by road was 5572 miles, her fuel consumption averaged 31 mpg, and her fuel was pure isooctane (C_8H_{18}, density = 0.6919 g/mL). How much energy was expended and how many tons of CO_2 were produced during her trip?

Answer

2.2×10^7 kJ; 1.6 tons of CO_2 (about twice as much as is released by flying)

Summary

Thermochemical concepts can be used to calculate the efficiency of various forms of fuel, which can then be applied to environmental issues. More than 80% of the energy used by modern society (about 3×10^{17} kJ/yr) is from the combustion of fossil fuels. Because of their availability, ease of transport, and facile conversion to convenient fuels, natural gas and petroleum are currently the preferred fuels. Supplies of **coal**, a complex solid material derived from plants that lived long ago, are much greater, but the difficulty in transporting and burning a solid makes it less attractive as a fuel. Coal releases the smallest amount of energy per gram of any fossil fuel, and natural gas the greatest amount. The combustion of fossil fuels releases large amounts of CO_2 that upset the balance of the **carbon cycle** and result in a steady increase in atmospheric CO_2 levels. Because CO_2 is a **greenhouse gas**, which absorbs heat before it can be radiated from Earth into space, CO_2 in the atmosphere can result in increased surface temperatures (the **greenhouse effect**). The temperature increases caused by increased CO_2 levels because of human activities are, however, superimposed on much larger variations in Earth's temperature that have produced phenomena

such as the ice ages and are still poorly understood.

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1.E: Fundamentals of Thermochemistry (Exercises)

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

Q1A

A sample of O_2 gas is under an external pressure of 17 atm and contained in a cylinder with a volume of 50 L. The gas is cooled and the resulting volume is 25 L. Calculate the amount of work done **on** the O_2 gas.

Solution

$$\begin{aligned} w &= -P\Delta V \\ &= -P_{\text{ext}}(V_2 - V_1) \\ &= -17atm\ (25\,L - 50\,L) = 425\,L\ atm \\ &= 425\ atm\ L\ (101.325\frac{J}{atm\ L}) \\ &= 43,063\,J \\ &= 43.06\,kJ \end{aligned}$$

Q1B

A system containing oxygen gas is heated at a constant pressure of 40.0 atm so that its volume increases 177 L to 458 L. Express the amount of work that the system did in kilo-joules.

Solution

The formula for work from the expansion of a gas at constant pressure

$$w = -P_{ext}\Delta V$$

$$w = -40\ atm \times (458\ L - 177\ L) = -11240\ L\ atm$$

Convert from L atm to joules

$$-11240\ L\ atm \times 101.325\ \frac{J}{L\ atm} = -1138893\ J$$

Convert from J to kJ and round to get the final answer

$$-1138893\ J \times \frac{1\ kJ}{1000\ J} = -1140\ kJ$$

$$w = -1140\ kJ$$

Q2

The gas mixture inside one of the cylinders of an airplane expands against a constant external pressure of 5.00 atm because of the growing altitude, from an initial volume of 500 mL (at the end of the compression stroke) to the final volume of 1200 mL. Calculate the work done on the gas mixture during this process and express it in Joules.

Solution

$$w = -(5.00\ \text{atm})(1200\ \text{mL} - 500\ \text{mL})(\frac{1\ \text{L}}{1000\,\text{mL}})(101.3\,\frac{\text{J}}{\text{L}\times\text{atm}}) = -354.55\,\text{J}$$

Q3

The following events are based on a true story. A butcher for the local Chinese restaurant needs to defrost a large chunk of beef, which weights $50\ lb$ and is currently at $0°C$. He wants to accomplish this by is going out onto the street and repeatedly drop it onto the ground. Suppose the potential energy of the meat completely transforms into heat each time it hits the ground, and that energy can be calculated from

$$V = mg\Delta h$$

where m is mass of the object, g is the acceleration of gravity, and Δh is change in height. If the man is $5\ \text{ft}$ tall and he wants to get the meat to room temperature ($25°\text{C}$), how many times does he have to drop the piece of meat? Assume the environment has no effect on the meat, and that it does not lose any heat. (Specific Heat of the Meat: $0.25\frac{\text{J}}{\text{g}\,°\text{C}}$).

Solution

There are two steps to solve this equation. First, to find the amount of heat absorbed by the meat from one drop. Second, to find the total amount of heat needed to warm the meat up from $0°C$ to $25°C$.

To find the total amount of heat required to bring the meat from $0°C$ to $25°C$, the equation for calculating heat has to be used:

$$Q = mC_p\Delta T$$

The mass of the meat can be calculated via conversion from lb to g, and is as follows:

$$50lb \times 453.592\frac{g}{lb} = 22679.6g$$

The change in temperature is just the final temperature minus the initial, so it is just $25°C$.

Lastly, C_p is given. Plugging in all of these values gives:

$$Q = 22679.6g \times 0.25\frac{J}{g°C} \times 25°C = 141747.5J$$

Thus, $141747.5J$ is the total amount of heat needed to heat up the meat to $25°C$.

Now to find the amount of heat transferred into the meat from one drop. This utilizes the potential energy equation. The question mentions how to calculate the potential energy, and all potential energy is translated into heat. Therefore.

$$Q = V = mg\Delta h$$

The problem gives the mass, the acceleration of gravity is $9.8\frac{m}{s^2}$, and height. Therefore, since the potential energy for one drop is equal to the heat for one drop, the heat can be calculated as such:

$$Q = 22.6796kg \times 9.8\frac{m}{s^2} \times 1.524m = 338.724\frac{kg\ m^2}{s^2} = 338.724J$$

From there, since no heat is lost, it carries over for each drop. Therefore, the number of times he needs to drop the meat is found by simple division:

$$141747.5J \div 338.724J = 418.474drops$$

Thus, the drops needed is around 419.

Abstract: Calculate heat from $Q = mC_p\Delta T$ and $Q = V = mg\Delta h$. Divide the two.

Q4

Suppose you have a ball $(C_p = 0.85\frac{J}{g^oC})$ at 25°C, what will its final temperature be if the amount of work equal to dropping it down from a height of 86.6m is done to it ? $(g = 9.81\frac{m}{s^2})$

Solution

$$U = mg\Delta h \tag{1.E.1416}$$
$$= m_{ball} \cdot 86.6m \cdot 9.81\frac{m}{s^2} \tag{1.E.1417}$$
$$= 850m_{ball} \tag{1.E.1418}$$

If we assuming all the kinetic energy at the time of collision converts to heat, then

$$\Delta T = \frac{q}{Cp \cdot m_{ball}} \tag{1.E.1419}$$
$$= \frac{U}{C_p \cdot m_{ball}} \tag{1.E.1420}$$
$$= \frac{850m_{ball}}{85\frac{J}{g^oC} \cdot m_{ball}} \frac{1\,kg}{1,000\,g} \tag{1.E.1421}$$
$$= 1.0^{\circ}C \tag{1.E.1422}$$
$$T_{final} = 25^{\circ}C + 1^{\circ}C \tag{1.E.1423}$$
$$= 26^{\circ}C \tag{1.E.1424}$$

Q7A

The rule of Dulong and Petit shows that the molar heat capacities of most metallic elements group around a certain value “X” $\frac{J}{K\ mol}$ at 25°C. By first calculating and showing the molar heat capacities of metals rhenium, silver, lead, tungsten, copper, molybdenum and hafnium (given that the respective specific heat capacities of these metals are 0.14$\frac{J}{K\ g}$, 0.23$\frac{J}{K\ g}$, 0.13$\frac{J}{K\ g}$, 0.13$\frac{J}{K\ g}$, 0.39$\frac{J}{K\ g}$, 0.25$\frac{J}{K\ g}$ and 0.14$\frac{J}{K\ g}$), find the value of “X”. (hint: take the average value of the calculated molar heat capacities and round off value to nearest whole number).

Solution

To first find the molar heat capacities of each metal, multiply the molar mass of each metal by their specific heat capacities:

Molar heat capacity of:

$\text{Re} = 0.14\frac{J}{K\ g} \times 186.207\frac{g}{mol} = 26.068\frac{J}{K\ mol}$ $\text{Ag} = 0.23\frac{J}{K\ g} \times 107.868\frac{g}{mol} = 24.809\frac{J}{K\ mol}$ $\text{Pb} = 0.13\frac{J}{K\ g} \times 207.2\frac{g}{mol} = 26.936\frac{J}{K\ mol}$

calculate the average molar heat capacity:

Average molar heat capacity=$\frac{1}{7}(26.068\frac{J}{K\ mol} + 24.809\frac{J}{K\ mol} + 26.936\frac{J}{K\ mol} + 23.899\frac{J}{K\ mol} + 24.7829\frac{J}{K\ mol} + 23.99\frac{J}{K\ mol} + 24.988\frac{J}{K\ mol}) = 25.068\frac{J}{K\ mol}$

$$\text{W} = 0.13\frac{J}{K\ g} \times 183.84\frac{g}{mol} = 23.899\frac{J}{K\ mol}$$
$$\text{Cu} = 0.39\frac{J}{K\ g} \times 63.546\frac{g}{mol} = 24.7829\frac{J}{K\ mol}$$
$$\text{Mo} = 0.25\frac{J}{K\ g} \times 95.96\frac{g}{mol} = 23.99\frac{J}{K\ mol}$$
$$\text{Hf} = 0.14\frac{J}{K\ g} \times 178.49\frac{g}{mol} = 24.988\frac{J}{K\ mol}$$

Q7B

The specific heat capacities of metals aluminum, bismuth, copper, lead, and silver at 25°C are 0.900, 0.123, 0.386, 0.128, and $0.233\frac{J}{g\ K}$. Calculate the molar heat capacities of these metals. According to the rule of Dulong and Petit, the molar heat capacities of metallic elements, like these, are approximately $25\frac{J}{K\ mol}$.

Solution

Multiply each of the specific heat capacities by its corresponding molar mass to obtain their molar heat capacities.

Aluminum:

$$0.900\frac{J}{g\ K} \times 26.98\frac{g}{mol} = 24.3\frac{J}{mol\ K}$$

Bismuth:

$$0.123\frac{J}{g\ K} \times 208.98\frac{g}{mol} = 25.7\frac{J}{mol\ K}$$

Copper:

$$0.386\frac{J}{g\ K} \times 63.55\frac{g}{mol} = 24.5\frac{J}{mol\ K}$$

Lead:

$$0.128\frac{J}{g\ K} \times 207.2\frac{g}{mol} = 26.5\frac{J}{mol\ K}$$

Silver:

$$0.223\frac{J}{g\ K} \times 107.87\frac{g}{mol} = 25.1\frac{J}{mol\ K}$$

Q9

An undisclosed volume of water is tightly sealed in a microwave-safe container at room temperature before it is placed in an ice bath where it is cooled by a student.

a. During the cooling process within the ice bath, state whether (ΔU), Q, and *W* of the system are negative, zero, or positive. Explain your reasoning.
b. After being cooled, the student decides that the water seems too cold so it is placed in the microwave where the container of water is heated back to room temperature. What are the new signs of (ΔU), Q, and *W* during the heating process? Explain your reasoning.
c. Now determine the signs of ($\Delta U_1 + \Delta U_2$), ($Q_1 + Q_2$) , and ($W_1 + W_2$), where possible, assuming that the cooling process was step 1 and the heating process was step 2.

Solution

a. *W* is *zero*, Q is *negative*, and (ΔU) is *negative*. Work is zero for this step because neither volume nor pressure of the container is changing. Since the water is cooler than before heat has left the system so it is negative; and because (ΔU) = Q + *W* and *W* = 0 then (ΔU) = Q which is negative so, (ΔU) is negative.
b. *W* is *zero*, Q is *positive*, and (ΔU) is *positive*. Work is zero for this step because neither volume nor pressure of the container is changing. Since the water is hotter than before heat has entered the system so it is positive and because (ΔU) = Q + *W* and *W* = 0 then (ΔU) = Q which is positive so, (ΔU) is positive.
c. Since *W* was equal to zero for both processes above (W_1 + W_2) is equal to *zero*. ($(\Delta U)_1$ + $(\Delta U)_2$) = (Q_1 + Q_2) where they are both equal to *zero*.

If the water is cooled from room temperature to a lower temperature and then heated directly back to room temperature, wouldn't ($(\Delta U)_1$ + $(\Delta U)_2$) be 0? Q is the only factor actually changing here and q(heating to cooling) = -q(cooling to heating) provided the change in t is the same. So both ($(\Delta U)_1$ + $(\Delta U)_2$) and q should be 0.

Q11A

Your lab partner slipped a sample of unknown hot metal that is 40.0g, which is initially at 130.0°C into a 100.0 g water that is initially at 50.0°C. A temperature probe indicates that equilibrium is reached at 60.15°C. Using the specific heat capacity of water 4.18$\frac{J}{K}$, calculate the specific heat capacity of the unknown metal.

Solution

Imagine two sub-systems: the metal and the water. If mixing the hot metal and cool water inside a well-insulated container (that prevent leaks of heat), then the heat absorbed by the system will equal zero. Since the system is the sum of the two sub-systems:

$$q_{\text{sys}} = 0 = q_{\text{metal}} + q_{\text{water}}$$

For both sub-systems, the amount of heat gained is equal to the specific heat capacity times the mass times the temperature change:

$$q_{\text{metal}} + q_{\text{water}} = m_{\text{water}} C_{s,\text{water}}\, \Delta T_{\text{metal}} = 0$$

Solving for the specific heat capacity of the metal:

$$c_{s,\text{metal}} = \frac{-m_{\text{water}} c_{s,\text{water}}\, \Delta T_{\text{water}}}{m_{\text{metal}} \Delta T_{\text{metal}}} = \frac{-100.0\ \text{g} \times 4.18 \frac{\text{J}}{\text{K g}} \times 10.15^{\circ}\text{C}}{40.0\ \text{g} \times -69.85^{\circ}\text{C}} = 1.52 \frac{\text{J}}{\text{K g}}$$

Tip: Do not convert Celsius to Kelvin. The Kelvin and Celsius scales differ only in their location of their zero points. Temperature change in Celsius is the same temperature change of Kelvin.

Q11B

Let's say you 34.5 grams of some hot metal that is initially at 75°C and you put that metal into 64.0 grams of water that is initially at 25°C. If the the two objects reach thermal equilibrium at 39°C, what is the specific heat capacity of the metal when the specific heat capacity of water is $4.18 \frac{J}{K\ g}$.

Solution

The formula used to solve this question is

$$m_1 c_1 \Delta T_1 = -m_2 c_2 \Delta T_2$$

Plug in your known values and solve for c_1

$$(34.15\ \ g)(c_1)(36\ ^{\circ}C) = -(64\ \ g)(4.18\ \ \frac{J}{K\ g})(-14\ ^{\circ}C)$$

$$c_1 = 3.02 \ \frac{J}{K\ g}$$

Q12

A 10.00 g sample of Aluminum at 60.0 °C and a 30.0 g sample of copper at a temperature of -20.0 °C were thrown simultaneously into a 50.0 g of water at a temperature of 25.0 °C. What will be the final temperature of the system consisting of the two metal samples and the water? Assuming that this system is completely isolated from the surroundings. Use the information below for your calculations.

- $c_{s(\mathrm{Al})} = 0.900 J/(K \cdot g)$
- $c_{s(\mathrm{Cu})} = 0.385 J/(K \cdot g)$
- $c_{s(\mathrm{H_2\ O})} = 4.184 J/(K \cdot g)$

Solution

Since our system is isolated, the thermal energy lost by one component is transferred to the other components.

$$q_1 = -q_2$$

which is equivalent to

$$C_1 \Delta T = -C_2 \Delta T$$

Noting that

$$C = mC_s$$

To avoid the complexity of handling three components, we can utilize the fact that temperature is a state function; we will simplify our calculations by choosing a different path to arrive to our final state.

We can do this in two steps:

Ignore the Aluminum sample and treat the copper and water as the only components of our system. After finding the equilibrium temperature, we add the Aluminum sample to the water and copper system, thereby reaching the same final state.

Which is the same answer we got before. This should make intuitive sense because regardless of the path we take, we end up with the exact same amount of thermal energy in our system.

Step 1

$$m_{\mathrm{Cu}} \times C_{s(\mathrm{Cu})} \times (T_f - T_{i(\mathrm{Cu})}) = -m_{\mathrm{H_2O}} C_{s(\mathrm{H_2\ O})} (T_f - T_{i(\mathrm{H_2\ O})})$$

$$30.0\,g \times 0.385\,J/(°C \cdot g) \times (T_f + 20°C) = -50.0\,g \times 4.184\,J/(°C \cdot g) \times (T_f - 25.0°C)$$

Solving for T_f for the copper and water system gives us

$$T_f = 22.6°C$$

Step 2

$$C_{(\mathrm{Cu+H_2\ O})} \times (T_f - T_{i(\mathrm{Cu+H_2\ O})}) = -m_{\mathrm{Al}} \times C_{s(\mathrm{Al})} \times (T_f - T_{i(\mathrm{Al})})$$

Noting that

$$C_{(\mathrm{Cu+H_2\ O})} = m_{\mathrm{H_2O}} \times C_{s(\mathrm{H_2\ O})} + m_{\mathrm{Cu}} \times C_{s(Cu)}$$

Combining the two equations and plugging the values gives us

$$[(30.0\,g \times 0.385\,J/(°C \cdot g)) + (50.0\,g \times 4.184\,J/(°C \cdot g))] \times (T_f - 22.6°C) = -10.0\,g \times 0.900\,J/(K \cdot g) \times (T_f - 60°C)$$

Solving for T_f:

$$T_f = 24.1°C$$

Which is the final temperature of the whole system.

Alternative Approach

We can also choose a path where we add the Aluminum first, and then we add the copper. Again, temperature is a state function and choosing a different path will not affect the final answer. We also show the calculation for this path for the sake of completion.

Step 1

$$m_{\mathrm{Cu}} \times C_{s(\mathrm{Al})} \times (T_f - T_{i(Al)}) = -m_{(\mathrm{H_2\,O})} \times C_{s(\mathrm{H_2\,O})} \times (T_f - T_{i(\mathrm{H_2\,O})})$$

$$10.0\,g \times 0.900\,J/(°C \cdot g) \times (T_f + 20°C) = -50.0\,g \times 4.184\,J/(°C \cdot g) \times (T_f - 25.0°C)$$

Solving for T_f for the aluminum and water system gives us

$$T_f = 26.4°C$$

Step 2

$$[(m_{(\mathrm{H_2\,O})} \times C_{s(\mathrm{H_2O})}) + (m_{\mathrm{Al}} \times C_{s(\mathrm{Al})})] \times (T_f - T_{i(\mathrm{Al+H_2\,O})}) = -m_{\mathrm{Al}} \times C_{s(\mathrm{Cu})} \times (T_f - T_{i(\mathrm{Cu})})$$

Plugging the numbers,

$$[(10.0\,g \times 0.900\,J/(°C \cdot g)) + (50.0\,g \times 4.184\,J/(°C \cdot g)] \times (T_f - 26.4°C) = -30.0\,g \times 0.385\,J/(K \cdot g) \times (T_f + 20°C)$$

Solving for T_f

$$T_f = 24.1°C$$

Q15A

Calculated the heat required to melt 3.00 g of ice and the heat required to change the temperature of water from 0°C to 100°C. What is the proportionality of the heat necessary to melt ice compared to the heat required to change the temperature of water from 0°C to 100°C? Use values from Table S2 and assume ΔH_f =334 J g^{-1} for calculations? Why is the heat positive instead of negative?

Solution

First lets determine the amount of heat needed to melt ice:

$$q = m\Delta H_f$$

$$q = 1,002\ \mathrm{J}$$

Next lets determine the heat required to raise the temperature of water 100°C:

$$q = mC_s\Delta T$$

$$q = 1,254\ \mathrm{J}$$

So the proportionality was determined to be 4:5

The heat is positive because the heat is required. The heat is needed to make the states go from solid to liquid when melting and then liquid to gas when the temperature is raised from 0 to 100 degrees Celsius.

Q15B

An observation in the 18th century stated that the heat that raised a certain mass of water from its freezing point to boiling point is equal to four-thirds of the heat required to melt the same mass of ice. Using the theory behind the observation, estimate the heat required to melt 10 g of ice, know that the heat capacity of water is 4.18 J/^{O}C.

Solution

Let the heat required to raise the temperature of water from its freezing point to its boiling point is q_1:

$$q = mc\Delta T \tag{1.E.1425}$$

$$m = \text{mass} \tag{1.E.1426}$$

$$c = 4.18\frac{J}{g\ ^oC} \tag{1.E.1427}$$

$$\Delta T = \text{freezing point} - \text{boiling point} = 100 - 0 = 100^oC \tag{1.E.1428}$$

$$q_1 = (10g)(4.18\frac{J}{g\ ^oC})(100^oC) \tag{1.E.1429}$$

$$q_1 = 4180\,\text{J} = 4.18\,\text{kJ} \tag{1.E.1430}$$

Let the heat required to melt 10 g of ice is q_2:

$$q_1 = \frac{4}{3}q_2 \tag{1.E.1431}$$

$$q_2 = \frac{3}{4}q_1 \tag{1.E.1432}$$

$$q_2 = \frac{3}{4}(4.18\,\text{kJ}) = 3.135\,\text{kJ} \tag{1.E.1433}$$

Q17

For his birthday, his John's parents have given him a compressible oven filled with 0.250 mol argon. If he sets this compressible oven at 1.00 atm and 273 K and let it contract from a constant external pressure of 0.100 atm until the gas pressure reaches 10.00 atm and the temperature reaches 400 K, what is the work done on the gas, the internal energy change, and the heat absorbed by the gas?

Solution

Using the ideal gas law $PV = nRT$, we can see that:

$$V_o = \frac{nRT_o}{P_o}$$

$$V_f = \frac{nRT_f}{P_f}$$

n = 0.25 mol, R = $0.082\frac{atm\ L}{mol\ K}$ Po = 1 atm, Pf = 10 atm To= 273K Tf = 400K

where V_o and V_f represent the initial and final volume of the chamber. Now, the pressure clearly changes inside the chamber, but outside the chamber, the pressure is held constant, so from the perspective of the surroundings:

$$W = -P(V_f - V_o)$$

where P represents the constant external pressure. Now substituting in V_f and V_o we can see that we've solved for work. Now, for any thermodynamic process:

$$\Delta U = \frac{3}{2} nR(T_f - T_o)$$

So plugging in those values allows us to solve for ΔU. Now, for heat, we simply subtract W from ΔU, by the first law of thermodynamics.

First law of thermodynamics: the total energy of an isolated system is a constant, energy can be transformed from one form to another, but it can not be created or destroyed.

The solution is incomplete.

Q19

Take 4 moles of ideal, monatomic gas going through expansion processes. The gas was initially put at a pressure of 5.00 atm and a temperature of 30°C. The gas first goes through isothermal expansion until the volume doubled. An isochoric process follows as the pressure is halved. $C_v = \frac{3}{2} R$

a. Build ΔU, W, and Q table for each process.
b. Find the final temperature.

Solution

Isothermal Process:

$$\Delta U = 0 \tag{1.E.1434}$$

$$W = Q \tag{1.E.1435}$$

$$W = nRT \ln\left(\frac{V_f}{V_i}\right) = (4\,\text{mol})(8.314\,\text{J}\cdot\text{K}^{-1}\text{mol}^{-1})(303.15\,\text{K})\ln(2) = 6988\,\text{J} = Q \tag{1.E.1436}$$

Isochoric Process

$$W = 0 \tag{1.E.1437}$$

$$\Delta U = Q \tag{1.E.1438}$$

First find the initial pressure of this process.

Use ideal law to relate pressure to volume. $PV = nRT$, in which P is inversely proportional to V.

Thus, when volume is doubled, pressure is halved so $P_f = 2.50\ \text{atm}$. Now, find the final temperature of this process.

Once again, relate P to T using ideal gas law. T is found to be directly proportional to P. Thus, if the pressure is halved from 2.50 atm, the temperature must also be halved from 303.15K.

$\frac{1}{2}(303.15\ \text{K}) = 151.58\ \text{K}$

$$Q = nC_v\Delta T = (4.00\,\text{mol})(\frac{3}{2})(8.314\frac{\text{J}}{\text{K mol}})(-151.58K) = -7561\,\text{J} = \Delta U \tag{1.E.1439}$$

Processes	ΔU	Q	W
Isothermal	0	6988J	6988J
Isochoric	-7561J	-7561J	0

Q20

An apparatus is set up such that an ideal gas is released into vacuum by opening a stopcock, hence allowing it to freely expand (i.e., no external force is applied). Calculate ΔU of the system, and prove that the free expansion process is adiabatic i.e no heat transfer.

Solution

$$\Delta U = \frac{3}{2} nR\Delta T \tag{1.E.1440}$$

As the expansion is isothermal, i.e. it occurs without a change in temperature:

$$\Delta T = 0 \tag{1.E.1441}$$

Hence,

$$\Delta U = 0 \tag{1.E.1442}$$

and

$$\Delta U = q_p + w \tag{1.E.1443}$$

As the external force applied on the gas is zero, the work done by the gas is zero.

Hence,

$$0 = q_p + 0 \tag{1.E.1444}$$

$$q_p = 0 \tag{1.E.1445}$$

This proves that the process is adiabatic.

Q21

A 150 L vessel contains 8.00 moles of neon at 270 K is compressed adiabatically, so that there is no gain nor loss of any heat, and irreversibly until the final temperature is 470 K. Calculate the change in internal energy, the heat added to the gas, and the work done on the gas.

Solution

Since Ne is a monatomic ideal gas and the volume of the vessel remains constant, the heat capacity of Ne can be expressed as:

$$C_p = \frac{3}{2} \times R = \frac{3}{2} \times 8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}} = 12.47 \frac{\text{J}}{\text{K} \cdot \text{mol}} \tag{1.E.1446}$$

$$\Delta U = nC_p \Delta T \tag{1.E.1447}$$

$$\Delta U = 8.00 \times 12.47 \frac{\text{J}}{\text{K} \cdot \text{mol}} \times (470 - 2700)\ \text{K} = 19952\ \text{J} = 20.0\ \text{kJ} \tag{1.E.1448}$$

Since the vessel is adiabatically compressed, no heat is added, therefore $q = 0$

$$\Delta U = q + w \tag{1.E.1449}$$

$$20.0\ \text{kJ} = 0 + w \tag{1.E.1450}$$

$$w = 20.0\ \text{kJ} \tag{1.E.1451}$$

Q22

A gas expands at constant external pressure of 3.00 atm until its volume has increased by 9.00 to 15.00 L. During this process, it absorbs 800J of heat from the surroundings.

a. Calculate the energy change of the gas, ΔU
b. Calculate the work, *w*, done on the gas in an irreversible adiabatic (*q* = 0) process connecting the same initial and final state.

Solution

a)

$$\Delta U = q + w \tag{1.E.1452}$$

$$\Delta U = 800J + -((3.00\,\text{atm})(15.00\text{L} - 9.00\text{L})(101.3\frac{\text{J}}{\text{L atm}})) = -1023.4\text{J} \tag{1.E.1453}$$

b)

$$q = 0 \tag{1.E.1454}$$

$$\Delta U = w \tag{1.E.1455}$$

$$\Delta U = -((3.00\text{atm})(15.00\text{L} - 9.00\text{L})(101.3\frac{\text{J}}{\text{L atm}})) = -1823.4\text{J} \tag{1.E.1456}$$

Q23

Using the theorem of equipartition of energy, calculate the specific heat capacity at constant pressure C_p at 25°C and 1 atm for O_2 and CO. Compare the calculated values to the experimental data $(\text{O}_2 = 29.36, \text{CO} = 29.1)$ and thus calculate the percent of the experimental value that results from vibrational motions. Answer: The percent of C_p due to vibrational motions is 0.897% for O_2 and 0.141% for CO.

Solution

The equipartition theorem states that each degree of freedom in a molecule contributes to ½ RT to the molar internal energy of a gas. To solve this problem, the number of degrees of freedom DOF in each molecule must be identifies.

O_2 is a linear diatomic particle, thus it has 3 translational degrees of freedom and 2 rotational degrees of freedom. Since CO is a linear molecule it also has 3 translational and 2 rotational degrees of freedom. The molecules are at room temperature. Thus, it is assumed that there is no vibration in the bond (other than the zero point energy).

The low percentage of C_p due to vibrational modes in both molecules indicates that the vibrational motion is extremely small and can be neglected.

$$DOF(\text{O}_2) = f_t + f_r = 3 + 2 = 5$$

$$DOF(\text{CO}) = f_t + f_r = 3 + 2 = 5$$

Using the equation

$$U = (DOF) \cdot \left(\frac{1}{2}RT\right)$$

find the internal energy of each gaseous molecule.

$$U\left(\text{O}_2\right) = (5) \cdot \left(\frac{1}{2}RT\right)$$

Since O_2 and CO have the same degrees of freedom,

\[U\left(\ce{O_2} \right) = U\left(\ce{CO} \right) = \dfrac{5}{2}RT\nonumber \]

The internal energy is related to C_v by

$$C_v = \left(\frac{\partial U}{\partial T}\right) = \left(\frac{\partial \frac{5}{2}RT}{\partial T}\right) = \frac{5}{2}R$$

C_v is related to C_p by

$$C_p = C_v + R = \frac{5}{2}R + R = \frac{7}{2}R = \frac{7}{2} \times 8.314 \frac{J}{mol\ K} = 29.099 \frac{J}{mol\ K}$$

The percent of the experimental value that results from vibration motion is the difference between calculated and experimental value as a percentage of the experimental value.

$$\%\text{vibrational motion}(O_2) = \frac{\text{experimental value} - \text{calculated value}}{\text{experimental value}} \times 100\% = \frac{29.36 - 29.099}{29.099} \times 100\% = 0.897\%$$

$$\%\text{vibrational motion}(CO) = \frac{\text{experimental value} - \text{calculated value}}{\text{experimental value}} \times 100\% = \frac{29.14 - 29.099}{29.099} \times 100\% = 0.141\%$$

Q23B

Using the classical equipartition theorem, calculate the value of C_p at 298 K and 1 atm for $\mathrm{HF(g)}$ and $\mathrm{F_2(g)}$, assuming that their pressure is constant. Then compare your calculation with the experiment values of $29.13 \frac{\mathrm{J}}{\mathrm{K\ mol}}$ and $31.30 \frac{\mathrm{J}}{\mathrm{K\ mol}}$ respectively. What is the per cent of the measured value that arises from vibrational motions?

Solution

Diatomic molecules possess a total of 6 degrees of freedom:

- 3 degrees in **translational** motion
- 2 degrees in **rotational** motion
- 1 degree in their **vibrational** motions

$$6.11 \text{ for } \mathrm{F_2(g)} = 0.735R \tag{1.E.1457}$$

The differences are due to the fact that some quantized energy levels are not available at certain temperatures, in this case room temperature. This means that $\mathrm{HF_{(g)}}$ contributed only 0.004R of its experimental value of $29.13 \frac{\mathrm{J}}{\mathrm{K\ mol}}$ to the vibrational degree of freedom, which is 0.014%. $\mathrm{F2(g)}$ contributed 0.265R of its experimental value $31.30 \frac{\mathrm{J}}{\mathrm{K\ mol}}$, which is 0.847%.

Each translational and rotational degree of freedom contributes $\frac{R}{2}$ to the heat capacity of a gas, while each vibrational degree of freedom contributes $\frac{2R}{2}$ (=R). Therefore the predicted heat capacity (C_v) at a constant volume is:

$$C_v = 3 \times (\frac{R}{2}) + 2 \times (\frac{R}{2}) + 1 \times (\frac{2R}{2}) = 7(\frac{R}{2}) \tag{1.E.1458}$$

Since the question is asking for the heat capacity of these gases that are under a constant pressure, the result is multiplied by an additional $\frac{2R}{2}$ because the volume can change in order to keep the pressure constant. Therefore:

$$C_v = (\frac{2R}{2}) + (\frac{7R}{2}) = \frac{9R}{2} \tag{1.E.1459}$$

$$R = 8.3145 \frac{\mathrm{J}}{\mathrm{K\ mol}} \tag{1.E.1460}$$

$$C_p = \frac{9(8.3145 \frac{\text{J}}{\text{K mol}})}{2} = 37.41 \frac{\text{J}}{\text{K mol}} \tag{1.E.1461}$$

This is the calculated value for both of the two gases. Since the experiment values were $29.13 \frac{\text{J}}{\text{K mol}}$ for $\text{HF}\,(\text{g})$ and $31.30 \frac{\text{J}}{\text{K mol}}$ for $\text{F}_2\,(\text{g})$, the differences between the calculations were:

$$8.28 \text{ for } \text{HF}\,(\text{g}) = 0.996R \tag{1.E.1462}$$

Q25

a. Calculate the change of enthalpy when a 69-grams sample of zinc is heated from 753 K to 927 K at a constant pressure of 1 atm.
b. Calculate the change of enthalpy when 3 moles of butane are heated from 204 K to 258 K at a constant pressure of 1 atm.

Solution

a)

$q = mC_s\Delta T$

$m = 69 \text{ g}$

$\Delta T = 927 - 753 = 174 \text{ K}$

$C_{\text{s(zinc)}} = 0.39 \frac{\text{J}}{\text{g }^{\text{oC}}}$

$q = 69 \times 0.39 \times 174 = 4682.34 \text{ J} = 4.56 \text{ kJ}$

b)

$q = nC_p\Delta T$

$n = 3$

$\Delta T = 258 - 204 = 54 \text{ K}$

$C_p = 132.42$

$q = 3 \times 132.42 \times 54 = 21452.04 \text{ J} = 21.4504 \text{ kJ}$

Q31

What is the change in enthalpy when 8.19 grams of ethane (C_2H_6) vaporizes, assuming a normal boiling point and $\Delta H_{\text{vap}} = 14.72 \ \frac{\text{kJ}}{\text{mol}}$.

Solution

First, convert grams of ethane to moles:

$$(8.19 \ \cancel{g \ \text{C}_2\text{H}_6}) \left(\frac{1 \, mol}{30.07 \ \cancel{g \ \text{C}_2\text{H}_6}} \right) = 0.272 \, mol$$

This step is to match quantity units of ethane to those in the given value of $\Delta\text{H}_{\text{vap}}$.

Then, given the ΔH_{vap},

$$(0.272\ \cancel{mol\ C_2H_6})\left(\frac{14.72\ kJ}{1\ \cancel{mol\ C_2H_8}}\right) = 4.004\ kJ$$

$\Delta \mathrm{H} = 4.004\ \ kJ$

This value is the change in enthalpy, or thermodynamic energy, when the specified amount of ethane undergoes the above reaction.

Q33

The heat capacity C_p of ice is $38\frac{\mathrm{J}}{\mathrm{K\ mol}}$ and C_p of water is $75\frac{\mathrm{J}}{\mathrm{K\ mol}}$. A 24.0 g ice cube at -15 °C is placed into 120 g of water at room temperature (25°C). What is the temperature of the water when it reaches equilibrium?

Solution

$$q_{\text{ice}} = -q_{\text{water}} \tag{1.E.1463}$$

$$m_{\text{ice}}C_{\text{ice}}(T_f - T_{\text{ice}}) = -m_{\text{water}}C_{\text{water}}(T_f - T_{\text{water}}) \tag{1.E.1464}$$

$$\left(\frac{24g\ \text{ice}}{18.02\frac{g}{mol}}\right) \times (38\frac{J}{K\ mol}) \times (T_f - (-15^oC)) = -\left(\frac{120g\ \text{water}}{18.02\frac{g}{mol}}\right) \times (75\frac{J}{K\ mol}) \times (T_f - 25^oC) \tag{1.E.1465}$$

$$T_f = 21.316^oC \tag{1.E.1466}$$

Q35

Determine the change in enthalpy (ΔH) for the following chemical reaction

$$4\,\mathrm{NH_{3(g)}} + 5\,\mathrm{O_{2(g)}} \longrightarrow 4\,\mathrm{NO_{(g)}} + 6\,\mathrm{H_2O_{(g)}}$$

given that:

$$\mathrm{O_{2(g)}} + \mathrm{N_{2(g)}} \longrightarrow 2\,\mathrm{NO_{(g)}}\ \Delta H = +180.5\ \frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$2\,\mathrm{H_2O_{(g)}} \longrightarrow 2\,\mathrm{H_{2\,(g)}} + \mathrm{O_{2\,(g)}}\ \Delta H = +483.64\ \frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$3\,\mathrm{H_{2(g)}} + \mathrm{N_{2(g)}} \longrightarrow 2\,\mathrm{NH_{3(g)}}\ \Delta H = -92.22\ \frac{\mathrm{kJ}}{\mathrm{mol}}.$$

Solution

Using Hess's Law, we can obtain the ΔH for

$$4\,\mathrm{NH_{3(g)}} + 5\,\mathrm{O_{2(g)}} \rightleftharpoons 4\,\mathrm{NO_{(g)}} + 6\,\mathrm{H_2O_{(g)}}$$

by adding and modifying the other equations provided until they resemble the equation above.

[redacted] $\Delta H = +180.5\ \frac{kJ}{mol} \times (2)$

[redacted] $\Delta H = +483.64\ \frac{kJ}{mol}(-3)$

[redacted] $\Delta H = -92.22\ \frac{kJ}{mol} \times (-2)$

The above modifications simplify out to

$$2\,O_{2(g)} + 2\,N_{2(g)} \rightleftharpoons 4\,NO_{(g)}\ \Delta H = +361.0\ \frac{kJ}{mol}$$

$$6\,H_{2\,(g)} + 3\,O_{2\,(g)} \rightleftharpoons 6\,H_2O_{(g)}\ \Delta H = -1450.92\ \frac{kJ}{mol}$$

$$4\,NH_{3\,(g)} \rightleftharpoons 6\,H_{2\,(g)} + 2\,N_{2\,(g)}\ \Delta H = 184.4\ \frac{kJ}{mol}$$

Species that are common to both sides can be cancelled out.

$$2\,O_{2(g)} + \cancel{2N_{2(g)}} \rightleftharpoons 4\,NO_{(g)}\ \Delta H = +361.0\ \frac{kJ}{mol}$$

$$\cancel{6H_{2\,(g)}} + 3\,O_{2\,(g)} \rightleftharpoons 6\,H_2O_{(g)}\ \Delta H = -1450.92\ \frac{kJ}{mol}$$

$$4\,NH_{3\,(g)} \rightleftharpoons \cancel{6H_{2\,(g)}} + \cancel{2N_{2\,(g)}}\ \Delta H = 184.4\ \frac{kJ}{mol}$$

Finally, after adding the remaining specimens and the enthalpy change that occurs with them we have:

$$4\,NH_{3(g)} + 5\,O_{2(g)} \rightleftharpoons 4\,NO_{(g)} + 6\,H_2O_{(g)} \text{ with } \Delta H = -905.5\ \frac{kJ}{mol}$$

Q37

ΔH of $C_6H_6\,(g)$ from $C_6H_6\,(l)$ to its gaseous form is +33.9 kJ/mol. Which of these two substances absorbs off more heat when 10 lbs of the substance is burned? Which of these two substances require less energy when condensed to solid form?

Solution

An alternative way to view this is to inspect the reactions under comparison

$$2\,C_6H_6\,(g) + 15\,O_2\,(g) \longrightarrow 12\,CO_2\,(g) + 6\,H_2O\,(g)$$

vs.

$$2\,C_6H_6\,(l) + 15\,O_2\,(g) \longrightarrow 12\,CO_2\,(g) + 6\,H_2O\,(g)$$

Recognizing that the difference between these equations is

$$2\,C_6H_6\,(l) \longrightarrow 2\,C_6H_6\,(g)$$

The problem states that the ΔH of the conversion of $C_6H_6\,(g)$ to $C_6H_6\,(l)$ is positive, and therefore, is an endothermic process. Consequently, ten pounds of $C_6H_6\,(g)$ contains more enthalpy than 10 pounds of $C_6H_6\,(l)$. Since these will both produce carbon dioxide and water when burned, their products are of the same final energy level. As a result, $C_6H_6\,(g)$ will give off more energy than $C_6H_6\,(l)$ when burned and $C_6H_6\,(l)$ will require less energy to form a solid.

Q39

Calculate the enthalpy change under standard conditions for the reaction:

$$C_3H_6O\,(l) + 4\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 3\,H_2O\,(l)$$

given information below:

- $\Delta H°_{f,\,O_2(g)}$: 0 kJ/mol
- $\Delta H°_{f,\,CO_2\,(g)}$: -393.5 kJ/mol
- $\Delta H°_{f,\,H_2O(l)}$: -285.83 kJ/mol
- $\Delta H°_{f,\,C_3H_6O(l)}$: -248 kJ/mol

Solution

Hess' Law:

$$\Delta H^o_{rxn} = \sum \Delta H^o_{f,\,products} - \sum \Delta H^o_{f,\,reactants}$$

$\Delta H°_{rxn}$ = [**3** (-393.5 kJ/mol) + **3** (-285.83 kJ/mol)] - [(-248 kJ/mol) + **4** (0 kJ/mol)] = -1790 kJ/mol

Q47

A 10 gram sample of pure hydrogen is burned completely with excess oxygen to generate liquid water in a constant volume calorimeter at 25 °C. The amount of heat evolved is 1,420 kJ.

a. Write and balance the chemical equation for the combustion reaction.
b. Calculate the standard change in internal energy for the combustion of 1.00 mole hydrogen to liquid water.
c. Calculate the standard enthalpy change per mole of hydrogen for the same reaction as in part (a).
d. Calculate the standard enthalpy of formation per mole of hydrogen, using data for the standard enthalpies of formation of liquid water (Table T1).

Solution

a. $2\,\mathrm{H_2\,(g)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{H_2O\,(l)}$
b. $\Delta U^o = q_v = \dfrac{-1420\,kJ}{10/(1.008\times 2)g/mol} = -286.3\ kJ/(mol\ of\ H_2)$
c. $\Delta H^o_{rxn} = \Delta U^o + \Delta n_{gas} RT = -286.3\ kJ/(mol\ of\ H_2) + (2mol.\ of\ H_2)(-3)(8.314 J/K/mol)(298\ K) = -580\ kJ/mol$
d. $\Delta H^o_r xn = 2\Delta H^o_f\{\mathrm{H_2}\}$ so $\Delta H^o_f/2$.

A consequence of the constant-volume condition is that the heat released corresponds to q_v and thus to the internal energy change ΔU_{sys} rather than to ΔH_{sys} under constant pressure conditions.

$$\Delta U_{sys} = q_v$$

This comes from the definition of enthalpy

$$H_{sys} = U_{sys} + PV$$

and associated change

$$\Delta H_{sys} = \Delta U_{sys} + \Delta(PV)$$

or using the chain rule

[redacted]

which simplifies to

$$\Delta H_{sys} = \Delta U_{sys} + V\Delta P$$

If we assuming ideal gas law for the gases

$$PV = nRT$$

or

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

substituting this into the equation for enthalpy change gives the enthalpy change under *constant volume* conditions in terms of changing number of moles

$$\Delta H_{sys} = \Delta U_{sys} + \Delta n_g RT$$

or

$$\Delta H_{sys} = q_v + \Delta n_g RT$$

where Δn_g is the change in the number of moles of gases in the reaction.

Q49

Carbon dioxide (CO_2) is a common byproduct of the combustion of fossil fuels. Estimate the standard enthalpy of formation (ΔH_f) of carbon dioxide at 25°C, use Table T1.

Solution

First write the equation:

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

The bond enthalpies in Table T3 allows us to calculate ΔH ° because 2 C=O and 2 C-O bonds are formed:

$$\Delta H \text{ °} \approx 2 \text{ mol } (-192.0 \text{ kJ mol}^{-1}) + 2 \text{ mol } (-85.5) = -555 \text{ kJ}$$

Next we need to write the equations for "striping" the atoms from there standard state to single atoms. Each of the atomization has an enthalpy that was found in Table T1:

$$\mathrm{C(s) \longrightarrow C(g)}$$

$$\Delta H \text{ °} = 1 \text{ mol } (716.7 \text{ kJ mol}^{-1}) = 716.7 \text{ kJ}$$

$$\mathrm{O_2(g) \longrightarrow 2\,O(g)}$$

$$\Delta H \text{ °} = 2 \text{ mol } (249.2 \text{ kJ mol}^{-1}) = 498.4 \text{ kJ}$$

Combine the results of all three equations to calculate ΔH_f of 1 mol of CO_2:

$$-555 \text{ kJ} + 716.7 \text{ kJ} + 498.4 \text{ kJ} = 660.1 \text{ kJ}$$

This solution should be the same if finding the standard enthalpy of formation by using Table T1 which would be -393.5 kJ for one mole of CO_2. Since this question is not clear, it is better if the students answering this question to just use Table T1 which will just use the standard heat of formation for and then have the sum of products minus the sum of reactants = the answer. So the answer would be -393.5 kJ.

Q51

Given the table of average bond enthalpies shown below, estimate the enthalpy change ΔH ° for the following reaction:

$$\mathrm{2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)}$$

Bond	Bond Enthalpy (kJ/mol)
H−H	436
H−O	463
O=O	498

Solution

To calculate the total enthalpy change of the reaction, we use Hess's Law. Thus, the total enthalpy of formation is equal to the sum of the enthalpy of formation of the reactants and the enthalpy of formation for the products.

Step 1. ΔH_1 = the bond enthalpies of $2\,\mathrm{H_2\,(g)} + \mathrm{O_2\,(g)}$

$$= 2(\mathrm{H{-}H}) + (\mathrm{O{=}O})$$

$$= 2(436)\ \mathrm{kJ/mol} + 498\ \mathrm{kJ/mol}$$

$$= +1370\ \mathrm{kJ/mol}$$

Step 2. ΔH_2 = the bond enthalpies of $2\mathrm{H_2O}(l)$

$$= 2 \times 2(\mathrm{H{-}O})$$

$$= 4(463)\ \mathrm{kJ/mol}$$

$$= -1852\ \mathrm{kJ/mol}$$

Step 3. $\Delta H^\circ = \Delta H_1 + \Delta H_2$

$$= 1370\ \mathrm{kJ/mol} - 1852\ \mathrm{kJ/mol}$$

$$= -482\ \mathrm{kJ/mol}$$

*Note in Step 1, ΔH_1 is positive because the process of breaking the bonds into individual atoms is **always** an endothermic process while in Step 2, ΔH_2 is negative because the process of creating bonds out of the individual atoms is **always** an exothermic process.*

Q59

Two quantum states are separated by an energy of 0.6 × 10^{-21} J. Calculate the relative populations of the two quantum states at a temperature of 33°C.

Solution

The equation for the relative populations of two quantum states, P_2/P_1 is given by the equation

$$\frac{P_2}{P_1} = e^{-(E_2 - E_1)/k_B T}$$

Where E_2-E_1 is the energy difference between the two states, k_B is the Boltzmann constant, and T is the temperature.

Plug in the given values into the equation to reach the final answer.

$$\frac{P_2}{P_1} = e^{-(0.6 \cdot 10^{-21}\ \mathrm{J})/1.38 \cdot 10^{-23}\mathrm{K^{-1}}(298\ \mathrm{K}))}$$

$$\frac{P_2}{P_1} = 0.86$$

Q63

By utilizing the Harmonic Oscillator Model, calculate the relative population of the first energy state and the ground state, both at $278.15\ \mathrm{K}$, for $\mathrm{H_2}$. The force constant for $\mathrm{H_2}$ is $510 \frac{\mathrm{N}}{\mathrm{m}}$

Solution

A few pieces of information need to be understood before going about solving this equation. First, the question asks for the “relative population” of the first energy state at a given temperature $(278.15\ \mathrm{K})$ to the energy state at $0\ \mathrm{K}$. Recall that energy states are basically a way of saying that every chemical species (molecule, atom, etc.) can “have” a

specific (discreet) amount of energy. Each of these values are a “state”, and the lowest- value state can be considered the “ground state”, and all states above are “excited states”. Also recall that the states can be named by quantum number; i.e if n were the quantum number, than the ground state would be $n = 0$ and the first state after that, an excited state, has a quantum number $n = 1$. The next step is to understand what “relative population is”. Basically, this refers to the probability that the species, in this case H_2, will be found in one energy state versus another. The equation that describes the probability of a species being in energy level n is as follows:

$$P(n) = Ce^{-\varepsilon_n/k_bT}$$

Where C is a constant, n is quantum number (energy level), k_b is Boltzmann’s constant, T is temperature, and ε is the energy of the molecule, which can be determined as such:

$$\varepsilon_n = \left(n + \frac{1}{2}\right) h\nu$$

$$h\nu = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

n, as already seen, is the quantum number. $h\nu$ in the equation for ε is defined as the product of planck’s constant (h) divided by 2π and the $\sqrt{\frac{k}{\mu}}$, where k is the force constant, which is given in the problem, and the μ is the *reduced mass*, which can be calculated as follows:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Where m is just the mass of each of the atoms. Since the mass of both hydrogens are 1 amu (u),

$$\mu = \frac{1 \times 1}{1 + 1} = \frac{1}{2}u$$

$$\frac{1}{2}u = 8.3027 \times 10^{-28} kg$$

Because the question is only interested in *relative* population, the actual number of molecules there are doesn’t really matter, since *relative* means to take the ratio between the probability of one energy state to another. Since the two energy states in comparison for this problem is $n = 1, n = 0$, (remember ground state is $n = 0$), the equation is as follows.

$$\frac{P(1) = Ce^{-\varepsilon_1/k_b 278.15\ \mathrm{K}}}{P(0) = Ce^{-\varepsilon_0/k_b 278.15\ \mathrm{K}}}$$

By simplification,

$$= e^{\dfrac{\varepsilon_1 - \varepsilon_0}{K_bT}}$$

And, substituting in the formula for energy(ε),

$$= e^{\dfrac{\left[\left(n + \frac{1}{2}\right) h\nu - \frac{1}{2}h\nu\right]}{K_bT}}$$

$$= e^{nh\nu/K_bT}$$

Here, $n = 1$ (because the 0 has already been taken into consideration) and $h\nu$ is as follows:

$$h\nu = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$h\nu = \frac{6.62607 \times 10^{-34} \frac{kgm^2}{s^2}}{2\pi} \sqrt{\frac{510 \frac{N}{m}}{8.3027 \times 10^{-28} kg}}$$

$$h\nu = \frac{6.62607 \times 10^{-34} Js^{-1}}{2\pi} \sqrt{\frac{510 \frac{N}{m}}{8.3027 \times 10^{-28} kg}}$$

$$h\nu = 8.2650 \times 10^{-20} J$$

All the variables have been found, so all there is left is to substitute and solve.

$$= e^{\frac{-(1)\left(8.2650 \times 10^{-20} J\right)}{1.3806 \times 10^{-23} \frac{m^2 kg}{s^2 K} (278.15 K)}}$$

$$= e^{\frac{-(1)\left(8.2650 \times 10^{-20} J\right)}{1.3806 \times 10^{-23} \frac{J}{K} (278.15 K)}}$$

$$\approx e^{-21.5229}$$

$$\approx 4.495 \times 10^{-10}$$

Thus, the probability of the H_2 molecules being in the 1st energy state when compared to the vibrational state of the lowest energy is $\approx 4.495 \times 10^{-10}$. This extremely low probability makes sense, because intuition says that the compound will most likely be found at its lowest energy.

Abstract: Find difference in energy, ε, divide by Boltzmann's constant (K_b) and Temperature. Plug as e^x and solve.

Q69

A container holds 2 L of gas under 5.00 atm and a ball floating in 10 L of NaOH. As the volume of the gas expands to 20 L, the ball is turned upside down. This turn is caused by the temperature increase of the NaOH after the gas expands. Assuming that no heat is lost, the density of NaOH is 2.13 g/cm^3 and the specific heat is 4.184 J/g K, calculate the increase in temperature of the NaOH.

Solution

The "work" completed by the ball to turn equals the negative value of the work the gas absorbs.

w = -(-P (V_2-V_1))

w = -(-5 atm) (20-2) L

w = 90 atm L (101.325 J/ 1 atm L)

w = 9119.25 J

The work carried out by the ball by the NaOH (in order to turn the ball) correlates to the increase in 10 L of NaOH temperature .

10 L of NaOH (1000 mL/1 L) = 10000 mL = 10000 cm^3 (2.13 g/cm^3) = 21300 g of NaOH

q = mC_pΔT

ΔT = (q NaOH) / (Specific Heat NaOH * g NaOH)

ΔT = (9119.25 J) / (4.184 J/K g)(21300 g)

ΔT = 0.102 K gained by the NaOH to turn the ball

Q69

Some gas in a piston expands against a constant pressure of 1.2 atm from a volume of 3 L to 18 L. The piston turns an egg beater submerged in 150 g of water. If the water was originally at 25°C, what is its temperature once the gas stops expanding? Assume that all of heat goes into the water and the specific heat capacity of water is 4.184 J K^{-1} g^{-1}.

Solution

From the first law of thermodynamics

$$\Delta U = q + w$$

In this case,$\Delta U = 0$, so

$$q = w = P_{ext}\Delta V = P_{ext}(V_f - V_i)$$

$$q = (1.2\ \text{atm})(18\ \text{L} - 3\ \text{L}) = 14.4\ \text{L atm}$$

Convert From L atm to joules using the conversion factor

$$14.4\ \text{L atm} \times 101.325\ \text{J L}^{-1}\text{atm}^{-1} = 1459\ \text{J}$$

Now connect the heat transferred to the temperature increased via the specific heat c_{sp} via

$$q = mc_{sp}\Delta T$$

$$\Delta T = \frac{q}{mc_{sp}}$$

$$\Delta T = \frac{1459\ \text{J}}{(150\ \text{g})(4.184\ \text{J K}^{-1}\text{g}^{-1})} = 2.325\ \text{K}$$

Since initial temperatures is 25° = 298 K so

$$T_f = 298\ K + 2.325\ \text{K}$$

$$T_f = 300.325\ K = 27.325°\text{C}$$

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2.1: The Nature of Spontaneous Processes

Learning Objectives

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

In this section, consider the differences between two types of changes in a system: Those that occur spontaneously and those that occur only with the continuous input of energy. In doing so, we'll gain an understanding as to why some systems are naturally inclined to change in one direction under certain conditions. We'll also gain insight into how the spontaneity of a process affects the distribution of energy and matter within the system.

Spontaneous and Nonspontaneous Processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. A spontaneous process is one that occurs naturally under certain conditions. A nonspontaneous process, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure 2.1.1).

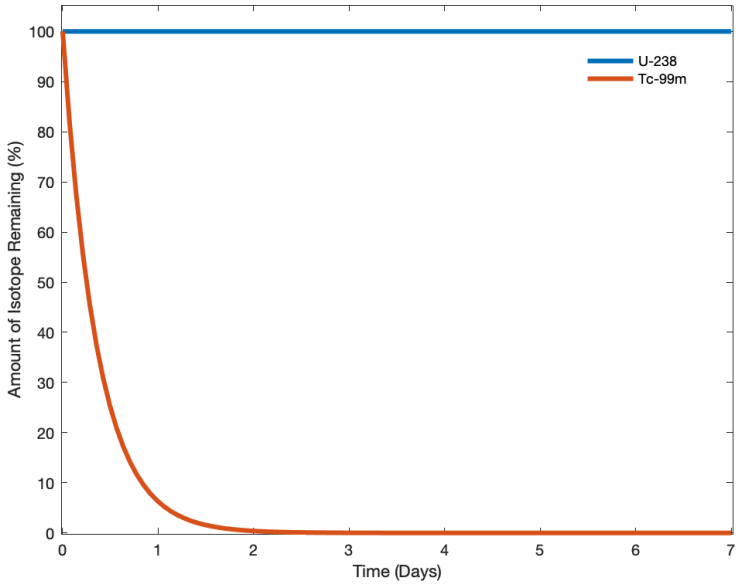


Figure 2.1.1: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts)

Two curves are shown to represent U-238 and Tc-99m respectively. The vertical axes represents the percentage of isotope remaining and the horizontal axes is the time that has elapsed in days.

As another example, consider the conversion of diamond into graphite (Figure 2.1.2).

[redacted]

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow, and so for all practical purposes diamonds are indeed "forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

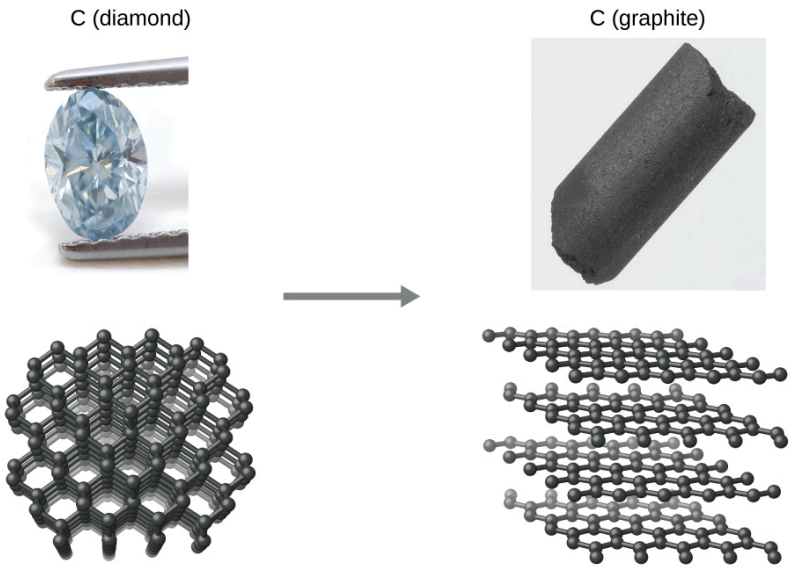


Figure 2.1.2: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

Comparison of diamond and graphite shown in its physical form as well as its molecular arrangement respectively.

Dispersal of Matter and Energy

As we extend our discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas on the left and a vacuum on the right (Figure 2.1.3). When the valve is opened, the gas spontaneously expands to fill both flasks. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

[redacted]

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.

[redacted]

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the movement of the gas appears to be related to the greater, more *uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous process took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

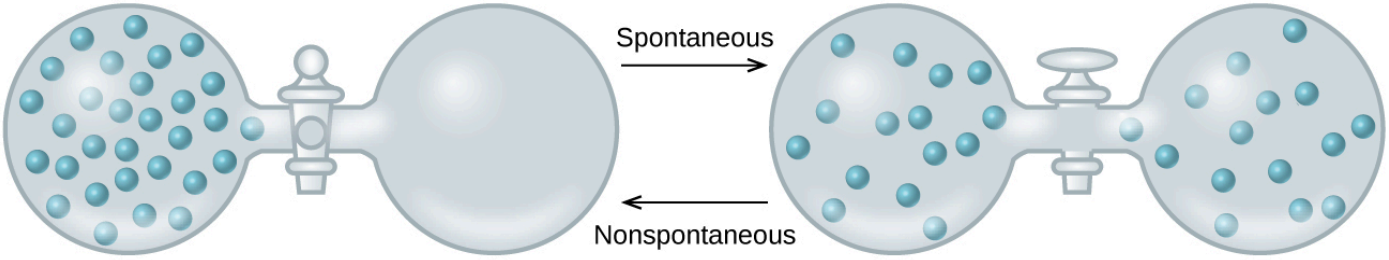


Figure 2.1.3: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

When the valve is closed, all of the gas molecules accumlating only in one side of the flask. The diagram with the open valve shows gas being equally distributed among the two flasks. The dispersion of the gas is labeled as spontaneous while the reverse is labeled as non spontaneous.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure 2.1.4). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

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

Two separated blocks. One is labeled X and the other labeled Y. The diagram next to it shows the two blocks in contact with one another.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

Example 2.1.1: Redistribution of Matter during a Spontaneous Process

Describe how matter and energy are redistributed when the following spontaneous processes take place:

a. A solid sublimes.
b. A gas condenses.
c. A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution



Figure 2.1.5:(credit a: modification of work by Jenny Downing; credit b: modification of work by "Fuzzy Gerdes"/Flickr; credit c: modification of work by Sahar Atwa)

This figure has three photos labeled, "a," "b," and "c." Photo a shows a glass with dry ice in water. There is a thick vapor coming from the top of the glass. Photo b shows water forming outside of a glass containing cold beverage. Photo c shows a sealed container that holds a red liquid.

a. *Sublimation* is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition. However, an input of energy from the surroundings ss required for the molecules to leave the solid phase and enter the gas phase.
b. *Condensation* is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition. As the gas molecules move together to form the droplets of liquid, they form intermolecular forces and thus release energy to the surroundings.
c. The process in question is *dilution*. The food dye molecules initially occupy a much smaller volume (the drop of dye solution) than they occupy once the process is complete (in the full glass of water). The process therefore entails a greater dispersal of matter. The process may also yield a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop, zero in the water), and the final state of the system contains a single dye concentration throughout. This process can occur with out a change in energy because the molecules have kinetic energy relative to the temperature of the water, and so will be constantly in motion.

Exercise 2.1.1

Describe how matter and energy are redistributed when you empty a canister of compressed air into a room.

Answer

This process entails both a greater and more uniform dispersal of matter as the compressed air in the canister is permitted to expand into the lower-pressure air of the room. The process also requires an input of energy to disrupt the intermolecular forces between the closely-spaced gas molecules that are originally compressed into the container. If you were to touch the nozzle of the canister, you would notice that it is cold because the exiting molecules are taking energy away from their surroundings, and the canister is part of the surroundings.

Summary

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will

experience a change in the way matter and/or energy is distributed within the system. In this section we have only discussed nuclear decay, physical changes of pure substances, and macroscopic events such as water flowing downhill. In the following sections we will discuss mixtures and chemical reactions, situations in which the description of sponteneity becomes more challenging.

Glossary

nonspontaneous process
: process that requires continual input of energy from an external source

spontaneous change
: process that takes place without a continuous input of energy from an external source

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II: PRINCIPLES OF THERMODYNAMICS (ENTROPY AND GIBBS ENERGY)

The term **thermodynamics** is actually something of a misnomer. At first glance, it suggests the study of systems in motion or undergoing change. In reality, classical thermodynamics is primarily concerned with systems at **equilibrium**. These are states in which no net change is occurring. The study of how systems evolve over time and approach equilibrium belongs instead to **kinetics** or **dynamics**. From this perspective, a more descriptive name for the subject might be *thermostatics*. Of course, after more than 150 years of widespread use, the name *thermodynamics* is firmly established, so we will embrace the historical terminology while recognizing that it is not entirely accurate.

2.1: The Nature of Spontaneous Processes

2.2: Entropy and Spontaneity - A Molecular Statistical Interpretation

2.3: Entropy and Heat - Experimental Basis of the Second Law of Thermodynamics

2.4: Entropy Changes and Spontaneity

2.5: Entropy Changes in Reversible Processes

2.6: Quantum States, Microstates, and Energy Spreading

2.7: The Third Law of Thermodynamics

2.8: Gibbs Energy

2.E: Principles of Thermodynamics (Exercises)

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2.2: Entropy and Spontaneity - A Molecular Statistical Interpretation

Learning Objectives

- The Learning Objective of this Module is to understand the relationship between internal energy and entropy.

We know that the first law of thermodynamics governs changes in the state function we called internal energy (U) and that changes in the internal energy (ΔU) are closely related to changes in the enthalpy (ΔH), which is a measure of the heat flow between a system and its surroundings at constant pressure. You also learned previously that the enthalpy change for a chemical reaction can be calculated using tabulated values of enthalpies of formation. This information, however, does not tell us whether a particular process or reaction will occur spontaneously.

Spontaneous Reactions

Let's consider a familiar example of spontaneous change. If a hot frying pan that has just been removed from the stove is allowed to come into contact with a cooler object, such as cold water in a sink, heat will flow from the hotter object to the cooler one, in this case usually releasing steam. Eventually both objects will reach the same temperature, at a value between the initial temperatures of the two objects. This transfer of heat from a hot object to a cooler one obeys the first law of thermodynamics: energy is conserved.

Now consider the same process in reverse. Suppose that a hot frying pan in a sink of cold water were to become hotter while the water became cooler. As long as the same amount of thermal energy was gained by the frying pan and lost by the water, the first law of thermodynamics would be satisfied. Yet we all know that such a process cannot occur: heat always flows from a hot object to a cold one, never in the reverse direction. That is, by itself the magnitude of the heat flow associated with a process does not predict whether the process will occur spontaneously.

For many years, chemists and physicists tried to identify a single measurable quantity that would enable them to predict whether a particular process or reaction would occur spontaneously. Initially, many of them focused on enthalpy changes and hypothesized that an exothermic process would always be spontaneous. But although it is true that many, if not most, spontaneous processes are exothermic, there are also many spontaneous processes that are not exothermic. For example, at a pressure of 1 atm, ice melts spontaneously at temperatures greater than 0°C, yet this is an endothermic process because heat is absorbed. Similarly, many salts (such as NH_4NO_3, NaCl, and KBr) dissolve spontaneously in water even though they absorb heat from the surroundings as they dissolve (i.e., $\Delta H_{soln} > 0$). Reactions can also be both spontaneous and highly endothermic, like the reaction of barium hydroxide with ammonium thiocyanate shown in Figure $2.2.1$.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

https://www.youtube.com/embed/GQkJI-Nq3Os?vq=hd1080

Figure 2.2.1: An Endothermic Reaction. The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic, so water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes place in the flask freezes water that has been placed under the beaker, so the flask becomes frozen to the wood. For a full video: see www.youtube.com/watch?v=GQkJI-Nq3Os.

Thus enthalpy is not the only factor that determines whether a process is spontaneous. For example, after a cube of sugar has dissolved in a glass of water so that the sucrose molecules are uniformly dispersed in a dilute solution, they never spontaneously come back together in solution to form a sugar cube. Moreover, the molecules of a gas remain evenly distributed throughout the entire volume of a glass bulb and never spontaneously assemble in only one portion of the available volume. To help explain why these phenomena proceed spontaneously in only one direction requires an additional state function called entropy (S), a thermodynamic property of all substances that is proportional to their degree of disorder.

> The direction of a spontaneous process is not governed by the internal energy change nor enthalpy change and thus the First Law of Thermodynamics cannot predict the direction of a natural process

Probabilities and Microstates

Chemical and physical changes in a system may be accompanied by either an increase or a decrease in the disorder of the system, corresponding to an increase in entropy ($\Delta S > 0$) or a decrease in entropy ($\Delta S < 0$), respectively. As with any other state function, the change in entropy is defined as the difference between the entropies of the final and initial states:

$$\Delta S = S_f - S_i \tag{2.2.1468}$$

When a gas expands into a vacuum, its entropy increases because the increased volume allows for greater atomic or molecular disorder. The greater the number of atoms or molecules in the gas, the greater the disorder. The magnitude of the entropy of a system depends on the number of microscopic states, or microstates, associated with it (in this case, the number of atoms or molecules); that is, the greater the number of microstates, the greater the entropy.

How can we express disorder quantitatively? From the example of coins, you can probably see that simple statistics plays a role: the probability of obtaining three heads and seven tails after tossing ten coins is just the ratio of the number of ways that ten different coins can be arranged in this way, to the number of all possible arrangements of ten coins.



Using the language of molecular statistics, we say that a collection of coins in which a given fraction of its members are heads-up constitutes a *macroscopic state* of the system. Since we do not care which coins are heads-up, there are clearly numerous configurations of the individual coins which can result in this "macrostate". Each of these configurations specifies a *microscopic state* of the system. The greater the number of microstates that correspond to a given macrostate (or configuration), the greater the probability of that macrostate. To see what this means, consider the possible outcomes of a toss of four coins (Table 2.2.1):

Table 2.2.1: Coin Toss Results

macrostate (Configuration)	ways	probability	microstates
0 heads	1	1/16	TTTT
1 head	4	4/16 = 1/4	HTTT THTT TTHT TTTH
2 heads	6	6/16 = 3/8	HHTT HTHT HTTH THHT TTHH THTH
3 heads	4	4/16 = 1/4	HHHT HTHH HHTH THHH
4 heads	1	1/16	HHHH

A toss of four coins will yield one of the five outcomes (macrostates) listed in the leftmost column of the table. The second column gives the number of "ways"— that is, the number of head/tail configurations of the set of coins (the number of microstates)— that can result in the macrostate. The probability of a toss resulting in a particular macrostate is proportional to the number of microstates corresponding to the macrostate, and is equal to this number, divided by the total number of possible microstates (in this example, 2^4 =16). An important assumption here is that all microstates are equally probable; that is, the toss is a "fair" one in which the many factors that determine the trajectory of each coin operate in an entirely random way.

> The greater the number of **microstates** that correspond to a given **macrostate**, the greater the probability of that **macrostate**.

Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the number of *microstates* possible for the system. A microstate (Ω) is a specific configuration of the locations and energies of the atoms or molecules that comprise a system like the following:

[redacted]

Here *k* is the Boltzmann constant and has a value of 1.38×10^{-23} J/K.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

For processes involving an increase in the number of microstates, $\Omega_f > \Omega_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $\Omega_f < \Omega_i$, yield a decrease in system entropy, $\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

Consider the general case of a system comprised of *N* particles distributed among *n* boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in 2^4 = 16 different microstates as illustrated in Figure 2.2.2. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates (Equation 1.1.2), *the most probable distribution is therefore the one of greatest entropy*.

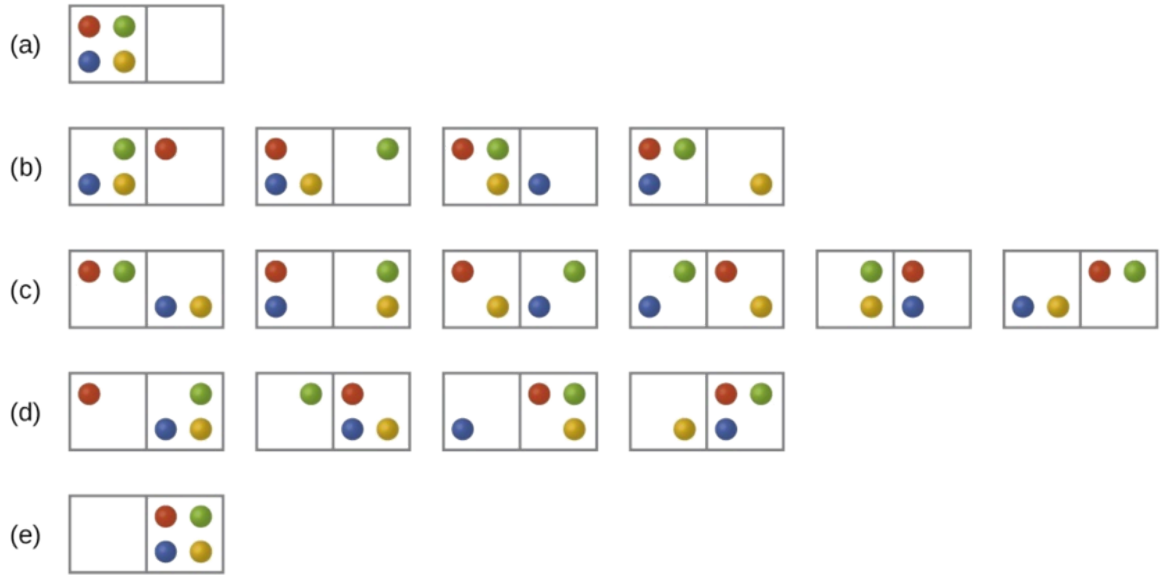


Figure 2.2.2: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is

$$\frac{6}{16} = \frac{3}{8}$$

The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of

$$\frac{1}{16}$$

The probability of finding all particles in only one box (either the left box or right box) is then

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

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

The previous description of an ideal gas expanding into a vacuum is a macroscopic example of this particle-in-a-box model.

For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. The spontaneous process whereby the gas contained initially in one flask expands to fill both flasks equally therefore yields an increase in entropy for the system.

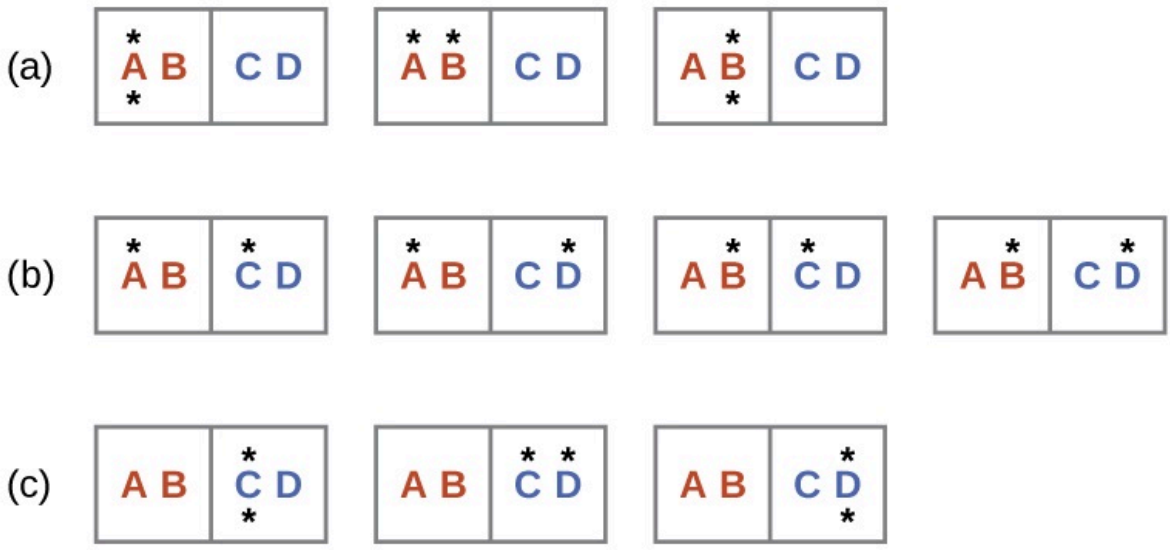


Figure 2.2.3: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles A and B contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of energy (represented as "*") in Figure 2.2.3. The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. And so, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. As for the previous example of matter dispersal, extrapolating this treatment to macroscopic collections of particles dramatically increases the probability of the uniform distribution relative to the other distributions. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects' temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

Example 2.2.1: Determination of ΔS

Consider the system shown here. What is the change in entropy for a process that converts the system from distribution (a) to (c)?



Solution

We are interested in the following change:

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

$$\begin{aligned}\Delta S &= k \ln \frac{\Omega_c}{\Omega_a} \\ &= 1.38 \times 10^{-23}\ J/K \times \ln \frac{6}{1} \\ &= 2.47 \times 10^{-23}\ J/K\end{aligned}$$

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

Exercise 2.2.1

Consider the system shown in Figure 2.2.3. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer

0 J/K

A disordered system has a greater number of possible microstates than does an ordered system, so it has a higher entropy. This is most clearly seen in the entropy changes that accompany phase transitions, such as solid to liquid or liquid to gas. As you know, a crystalline solid is composed of an ordered array of molecules, ions, or atoms that occupy fixed positions in a lattice, whereas the molecules in a liquid are free to move and tumble within the volume of the liquid; molecules in a gas have even more freedom to move than those in a liquid. Each degree of motion increases the number of available microstates, resulting in a higher entropy. Thus the entropy of a system must increase during melting ($\Delta S_{fus} > 0$). Similarly, when a liquid is converted to a vapor, the greater freedom of motion of the molecules in the gas phase means that $\Delta S_{vap} > 0$. Conversely, the reverse processes (condensing a vapor to form a liquid or freezing a liquid to form a solid) must be accompanied by a decrease in the entropy of the system: $\Delta S < 0$.

Definition: Entropy

Entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. The greater the number of possible microstates for a system, the greater the disorder and the higher the entropy.

Disorder is more probable than order because there are so many more ways of achieving it. Thus coins and cards tend to assume random configurations when tossed or shuffled, and socks and books tend to become more scattered about a teenager's room during the course of daily living. But there are some important differences between these large-scale mechanical, or macro systems, and the collections of sub-microscopic particles that constitute the stuff of chemistry, and which we will refer to here generically as **molecules**. Molecules, unlike macro objects, are capable of accepting, storing, and giving up energy in tiny amounts (quanta), and act as highly efficient carriers and spreaders of thermal energy as they move around. Thus, **in chemical systems**,

1. **We are dealing with huge numbers of particles**. This is important because statistical predictions are always more accurate for larger samples. Thus although for the four tosses there is a good chance (62%) that the H/T ratio will fall outside the range of 0.45 - 0.55, this probability becomes almost zero for 1000 tosses. To express this in a different way, the chances that 1000 gas molecules moving about randomly in a container would at any instant be distributed in a sufficiently non-uniform manner to produce a detectable pressure difference between the two halves of a container will be extremely small. If we increase the number of molecules to a chemically significant number (around 10^{20}, say), then the same probability becomes indistinguishable from zero.
2. **Once the change begins, it proceeds spontaneously.** That is, no external agent (a tosser, shuffler, or teenager) is needed to keep the process going. Gases will spontaneously expand if they are allowed to, and reactions, once started, will proceed toward equilibrium.

3. **Thermal energy is continually being exchanged between the particles of the system, and between the system and the surroundings.** Collisions between molecules result in exchanges of momentum (and thus of kinetic energy) amongst the particles of the system, and (through collisions with the walls of a container, for example) with the surroundings.
4. **Thermal energy spreads rapidly and randomly throughout the various energetically accessible microstates of the system.** The **direction** of spontaneous change is that which results in the maximum possible spreading and sharing of thermal energy.

The importance of these last two points is far greater than you might at first think, but to fully appreciate this, you must recall the various ways in which thermal energy is stored in molecules.

Sign of Entropy Change

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure 2.2.4. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{liquid} > S_{solid}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

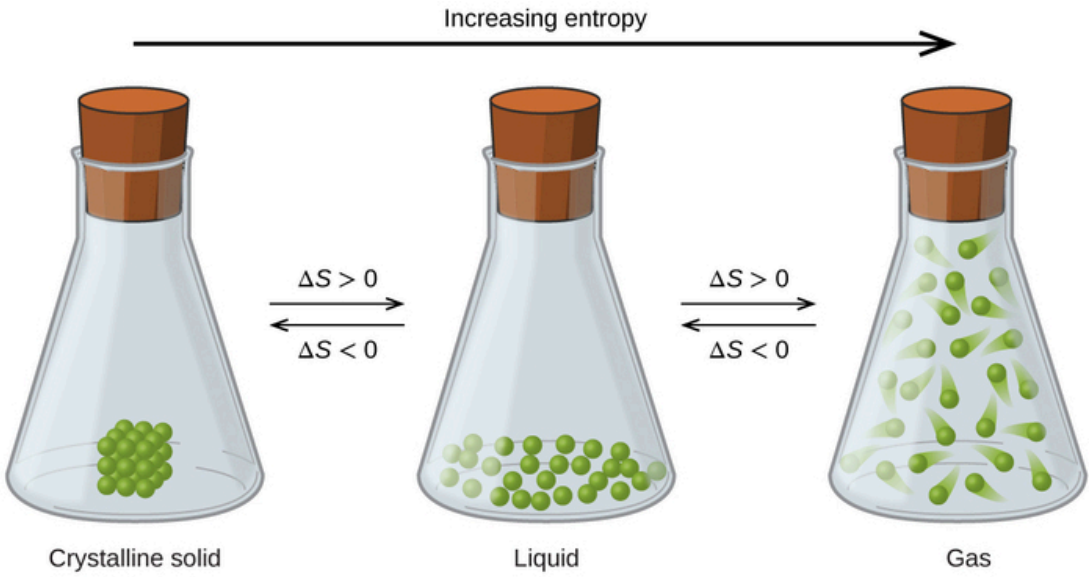


Figure 2.2.4: The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the vapor or gas phase. The atoms or molecules occupy a *much* greater volume than in the liquid phase; therefore each atom or molecule can be found in many more locations than in the liquid (or solid) phase. Consequently, for any substance,

$$S_{gas} \gg S_{liquid} > S_{solid} \tag{2.2.1471}$$

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 2.2.5).

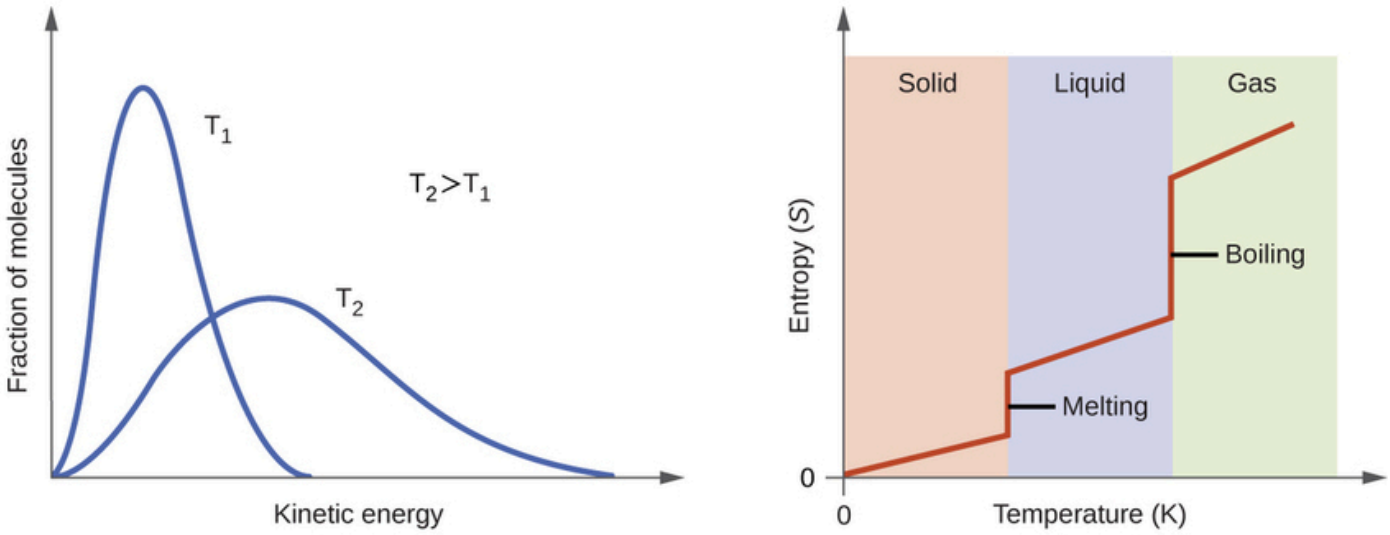


Figure 2.2.5: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

The entropy of a substance is influenced by structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (which is a topic beyond the scope of our treatment). For molecules, greater numbers of atoms (regardless of their masses) increase the ways in which the molecules can vibrate and thus the number of possible microstates and the system entropy.

Finally, variations in the types of particles affect the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in Example 2.2.2.

Example 2.2.2: Predicting the Sign of ΔS

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

a. One mole liquid water at room temperature $\longrightarrow$ one mole liquid water at 50 °C
b. $\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \longrightarrow \mathrm{AgCl}(s)$
c. $\mathrm{C_6H_6\,(l)} + \frac{15}{2}\,\mathrm{O_2\,(g)} \longrightarrow 6\,\mathrm{CO_2\,(g)} + 3\,\mathrm{H_2O\,(l)}$
d. $\mathrm{NH_3}(s) \longrightarrow \mathrm{NH_3}(l)$

Solution

a. positive, temperature increases
b. negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter
c. negative, net decrease in the amount of gaseous species
d. positive, phase transition from solid to liquid, net increase in dispersal of matter

Exercise 2.2.2

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

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

Answer a

Positive; The solid dissolves to give an increase of mobile ions in solution.

Answer b

Negative; The liquid becomes a more ordered solid.

Answer c

Positive; The relatively ordered solid becomes a gas.

Answer d

Positive; There is a net production of one mole of gas.

Summary

Entropy (S) is a state function that can be related to the number of microstates for a system (the number of ways the system can be arranged) and to the ratio of reversible heat to kelvin temperature. It may be interpreted as a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the “disorder” of the system. For a given substance, $S_{solid} < S_{liquid} \ll S_{gas}$ in a given physical state at a given temperature, entropy is typically greater for heavier atoms or more complex molecules. Entropy increases when a system is heated and when solutions form. Using these guidelines, the sign of entropy changes for some chemical reactions may be reliably predicted.

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2.3: Entropy and Heat - Experimental Basis of the Second Law of Thermodynamics

Learning Objectives

- The Learning Objective of this Module is to understand the relationship between internal energy and entropy.

Thermodynamic Definition of Entropy

Experiments show that the magnitude of ΔS_{vap} is 80–90 J/(mol•K) for a wide variety of liquids with different boiling points. However, liquids that have highly ordered structures due to hydrogen bonding or other intermolecular interactions tend to have significantly higher values of ΔS_{vap}. For instance, ΔS_{vap} for water is 102 J/(mol•K). Another process that is accompanied by entropy changes is the formation of a solution. As illustrated in Figure 2.3.1, the formation of a liquid solution from a crystalline solid (the solute) and a liquid solvent is expected to result in an increase in the number of available microstates of the system and hence its entropy. Indeed, dissolving a substance such as NaCl in water disrupts both the ordered crystal lattice of NaCl and the ordered hydrogen-bonded structure of water, leading to an increase in the entropy of the system. At the same time, however, each dissolved $\mathrm{Na^+}$ ion becomes hydrated by an ordered arrangement of at least six water molecules, and the $\mathrm{Cl^-}$ ions also cause the water to adopt a particular local structure. Both of these effects increase the order of the system, leading to a decrease in entropy. The overall entropy change for the formation of a solution therefore depends on the relative magnitudes of these opposing factors. In the case of an NaCl solution, disruption of the crystalline NaCl structure and the hydrogen-bonded interactions in water is quantitatively more important, so $\Delta S_{soln} > 0$.

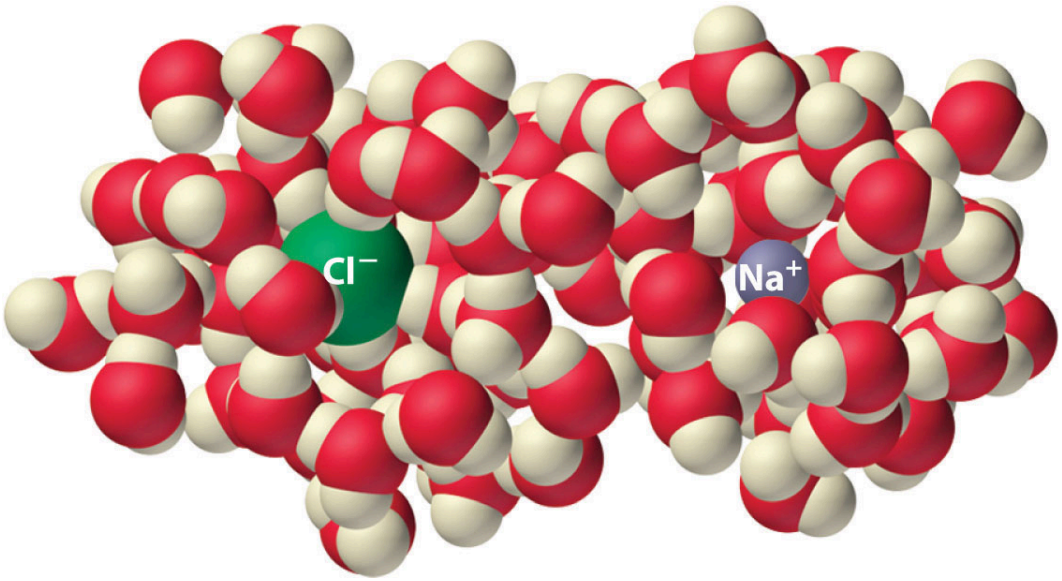


Figure 2.3.1: The Effect of Solution Formation on Entropy

Dissolving NaCl in water results in an increase in the entropy of the system. Each hydrated ion, however, forms an ordered arrangement with water molecules, which decreases the entropy of the system. The magnitude of the increase is greater than the magnitude of the decrease, so the overall entropy change for the formation of an NaCl solution is positive.

Example 2.3.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of $NH_3(g)$ or 1 mol of He(g), both at 25°C
b. 1 mol of Pb(s) at 25°C or 1 mol of Pb(l) at 800°C

Given: amounts of substances and temperature

Asked for: higher entropy

Strategy:

From the number of atoms present and the phase of each substance, predict which has the greater number of available microstates and hence the higher entropy.

Solution A

Both substances are gases at 25°C, but one consists of He atoms and the other consists of NH_3 molecules. With four atoms instead of one, the NH_3 molecules have more motions available, leading to a greater number of microstates. Hence we predict that the NH_3 sample will have the higher entropy.

Solution B

The nature of the atomic species is the same in both cases, but the phase is different: one sample is a solid, and one is a liquid. Based on the greater freedom of motion available to atoms in a liquid, we predict that the liquid sample will have the higher entropy.

Exercise 2.3.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of He(g) at 10 K and 1 atm pressure or 1 mol of He(g) at 250°C and 0.2 atm
b. a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm or a sample of 2 mol of $NH_3(g)$ at 25°C and 1 atm

Answer a

1 mol of He(g) at 250°C and 0.2 atm (higher temperature and lower pressure indicate greater volume and more microstates)

Answer b

a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm (more molecules of gas are present)

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2.4: Entropy Changes and Spontaneity

Learning Objectives

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

Connecting Entropy and Heat to Spontaneity

In the quest to identify a property that may reliably predict the spontaneity of a process, we have identified a very promising candidate: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S_{sys} > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

[redacted]

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \tag{2.4.1472}$$

and

[redacted]

The arithmetic signs of q_{rev} denote the loss of heat by the system and the gain of heat by the surroundings. Since $T_{sys} > T_{surr}$ in this scenario, the magnitude of the entropy change for the surroundings will be greater than that for the system, and so the sum of ΔS_{sys} and ΔS_{surr} will yield a positive value for ΔS_{univ}. *This process involves an increase in the entropy of the universe.*

2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \tag{2.4.1473}$$

and

[redacted]

The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*

3. The temperature difference between the objects is infinitesimally small, $T_{sys} \approx T_{surr}$, and so the heat flow is thermodynamically *reversible*. See the previous section's discussion). In this case, the system and surroundings experience entropy changes that are equal in magnitude and therefore sum to yield a value of zero for ΔS_{univ}. *This process involves no change in the entropy of the universe.*

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the second law of thermodynamics: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in Table 2.4.1.

Table 2.4.1: The Second Law of Thermodynamics

$\Delta S_{univ} > 0$	spontaneous
$\Delta S_{univ} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{univ} = 0$	reversible (system is at equilibrium)

Definition: The Second Law of Thermodynamics

All spontaneous changes cause an increase in the entropy of the universe, i.e.,

$$\Delta S_{\text{univ}} > 0. \tag{2.4.1474}$$

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:

[redacted]

We may use this equation to predict the spontaneity of a process as illustrated in Example 2.4.1.

Example 2.4.1: Will Ice Spontaneously Melt?

The entropy change for the process

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

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at –10.00 °C? Is it spontaneous at +10.00 °C?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = –6.00 kJ.

At –10.00 °C (263.15 K), the following is true:

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

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

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

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

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

Exercise 2.4.1

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of ΔS_{univ}?

Answer

Entropy is a state function, and freezing is the opposite of melting. At –10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, –0.9 J/K.

Summary

The second law of thermodynamics states that a *spontaneous* process increases the entropy of the universe, $S_{univ} > 0$. If $\Delta S_{univ} < 0$, the process is *nonspontaneous*, and if $\Delta S_{univ} = 0$, the system is at equilibrium.

Key Equations

- $\Delta S^\circ = \Delta S^\circ_{298} = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants})$
- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$

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2.5: Entropy Changes in Reversible Processes

Learning Objectives

You are expected to be able to define and explain the significance of terms identified in ***bold***.

- A ***reversible*** *process* is one carried out in infinitesimal steps after which, when undone, both the system and surroundings (that is, the world) remain unchanged (see the example of gas expansion-compression below). Although true reversible change cannot be realized in practice, it can always be approximated.
- As a process is carried out in a more reversible manner, the value of *w* approaches its maximum possible value, and *q* approaches its minimum possible value.
- Although *q* is not a state function, the quotient q_{rev}/T is, and is known as the *entropy*.

A change is said to occur reversibly when it can be carried out in a series of infinitesimal steps, each one of which can be undone by making a similarly minute change to the conditions that bring the change about. For example, the reversible expansion of a gas can be achieved by reducing the external pressure in a series of infinitesimal steps; reversing any step will restore the system and the surroundings to their previous state. Similarly, heat can be transferred reversibly between two bodies by changing the temperature difference between them in infinitesimal steps each of which can be undone by reversing the temperature difference.

The most widely cited example of an **irreversible** change is the free expansion of a gas into a vacuum. Although the system can always be restored to its original state by recompressing the gas, this would require that the surroundings perform work on the gas. Since the gas does no work on the surrounding in a free expansion (the external pressure is zero, so $P\Delta V = 0$,) there will be a permanent change in the surroundings. Another example of irreversible change is the conversion of mechanical work into frictional heat; there is no way, by reversing the motion of a weight along a surface, that the heat released due to friction can be restored to the system.

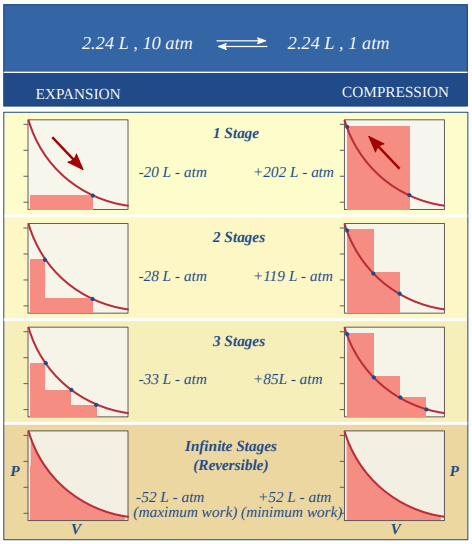


Figure 2.5.1: Reversible vs. Irreversible Expansions and Compressions. (CC BY-NC; Ümit Kaya)

These diagrams show the same expansion and compression ±ΔV carried out in different numbers of steps ranging from a single step at the top to an "infinite" number of steps at the bottom. As the number of steps increases, the processes become less irreversible; that is, the difference between the work done in expansion and that required to re-compress the gas diminishes. In the limit of an ”infinite” number of steps (bottom), these work terms are identical, and both the system and surroundings (the “world”) are unchanged by the expansion-compression cycle. In all other cases the system (the gas) is restored to its initial state, **but the *surroundings* are forever changed.**

Definition: Reversible Changes

A reversible change is one carried out in such as way that, when undone, both the system and surroundings (that is, the world) remain unchanged.

It should go without saying, of course, that any process that proceeds in infinitesimal steps would take infinitely long to occur, so thermodynamic reversibility is an idealization that is never achieved in real processes, except when the system is already at equilibrium, in which case no change will occur anyway! So why is the concept of a reversible process so important?

The answer can be seen by recalling that the change in the internal energy that characterizes any process can be distributed in an infinity of ways between heat flow across the boundaries of the system and work done on or by the system, as expressed by the First Law of thermodynamics

[redacted]

Each combination of *q* and *w* represents a different pathway between the initial and final states. It can be shown that as a process such as the expansion of a gas is carried out in successively longer series of smaller steps, the absolute value of *q* approaches a minimum, and that of *w* approaches a maximum that is characteristic of the particular process. Thus when a process is carried out reversibly, the *w*-term in Equation 2.5.981 has its greatest possible value, and the *q*-term is at its smallest. These special quantities w_{max} and q_{min} (which we denote as q_{rev} and pronounce "q-reversible") have unique values for any given process and are therefore state functions.

Work and Reversibility

Changes in entropy (ΔS), together with changes in enthalpy (ΔH), enable us to predict in which direction a chemical or physical change will occur spontaneously. Before discussing how to do so, however, we must understand the difference between a reversible process and an irreversible one. In a reversible process, every intermediate state between the extremes is an equilibrium state, regardless of the direction of the change. In contrast, an irreversible process is one in which the intermediate states are not equilibrium states, so change occurs spontaneously in only one direction. As a result, a reversible process can change direction at any time, whereas an irreversible process cannot. When a gas expands reversibly against an external pressure such as a piston, for example, the expansion can be reversed at any time by reversing the motion of the piston; once the gas is compressed, it can be allowed to expand again, and the process can continue indefinitely. In contrast, the expansion of a gas into a vacuum ($P_{ext} = 0$) is irreversible because the external pressure is measurably less than the internal pressure of the gas. No equilibrium states exist, and the gas expands irreversibly. When gas escapes from a microscopic hole in a balloon into a vacuum, for example, the process is irreversible; the direction of airflow cannot change.

Because work done during the expansion of a gas depends on the opposing external pressure ($w = P_{ext}\Delta V$), work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$. Whether a process is reversible or irreversible, the first law of thermodynamics holds (Equation 2.5.981). Because U is a state function, the magnitude of ΔU does not depend on reversibility and is independent of the path taken. So

[redacted]

Work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process:

$$w_{rev} \geq w_{irrev} \tag{2.5.1477}$$

In other words, ΔU for a process is the same whether that process is carried out in a reversible manner or an irreversible one. We now return to our earlier definition of entropy, using the magnitude of the heat flow for a reversible process (q_{rev}) to define entropy quantitatively.

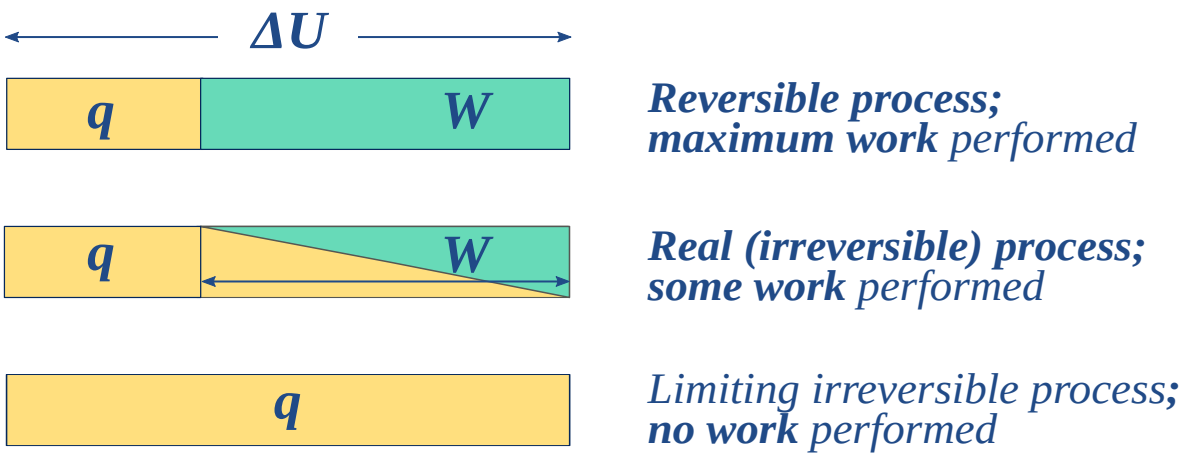


Figure 2.5.2: Note that the reversible condition implies w_{max} and q_{min}. The impossibility of extracting all of the internal energy as work is essentially a statement of the Second Law. (CC BY-NC; Ümit Kaya)

For a process that reversibly exchanges a quantity of heat q_{rev} with the surroundings, the entropy change is defined as

[redacted]

This is the basic way of evaluating ΔS for *constant-temperature processes* such as phase changes, or the isothermal expansion of a gas. For processes in which the temperature is not constant such as heating or cooling of a substance, the equation must be integrated over the required temperature range, as discussed below.

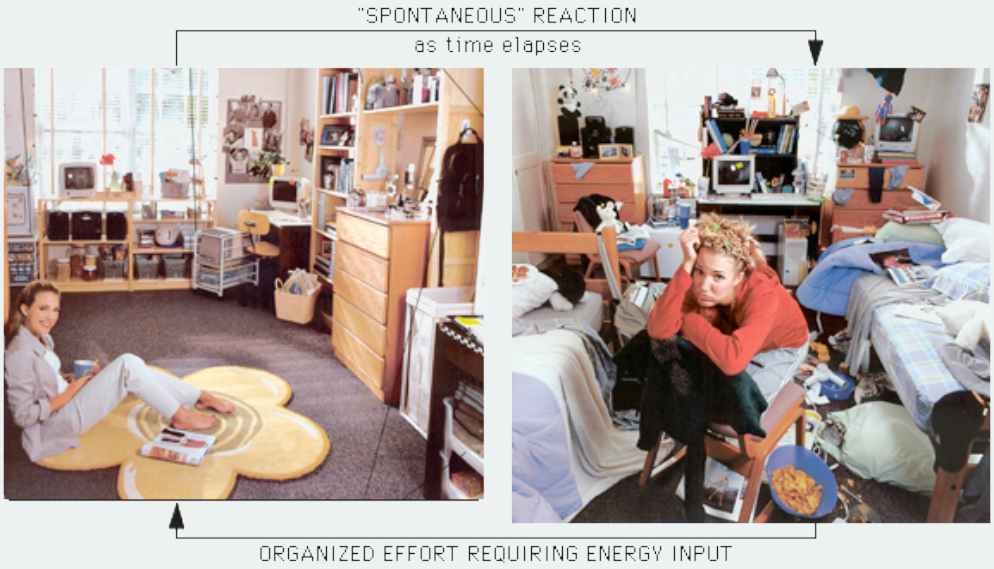
Q&A: If no real process can take place reversibly, what use is an expression involving q_{rev}?

This is a rather fine point that you should understand: although transfer of heat between the system and surroundings is impossible to achieve in a truly reversible manner, this idealized pathway is only crucial for the definition of ΔS; by virtue of its being a state function, the same value of ΔS will apply when the system undergoes the same net change via any pathway. For example, the entropy change a gas undergoes when its volume is doubled at constant temperature will be the same regardless of whether the expansion is carried out in 1000 tiny steps (as reversible as patience is likely to allow) or by a single-step (as irreversible a pathway as you can get!) expansion into a vacuum (Figure 2.5.1).

Entropy is an *extensive* quantity; that is, it is proportional to the quantity of matter in a system; thus 100 g of metallic copper has twice the entropy of 50 g at the same temperature. This makes sense because the larger piece of copper contains twice as many quantized energy levels able to contain the thermal energy.

Entropy and "disorder"

Entropy is still described, particularly in older textbooks, as a measure of disorder. In a narrow technical sense this is correct, since the spreading and sharing of thermal energy does have the effect of randomizing the disposition of thermal energy within a system. But to simply equate entropy with “disorder” without further qualification is extremely misleading because it is far too easy to forget that entropy (and thermodynamics in general) applies only to molecular-level systems capable of exchanging thermal energy with the surroundings. Carrying these concepts over to macro systems may yield compelling analogies, but it is no longer science. It is far better to avoid the term “disorder” altogether in discussing entropy.



ΔS_{sys} for an Isothermal Expansion (or Compression)

As a substance becomes more dispersed in space, the thermal energy it carries is also spread over a larger volume, leading to an increase in its entropy. Because entropy, like energy, is an extensive property, a dilute solution of a given substance may well possess a smaller entropy than the same volume of a more concentrated solution, but the entropy *per mole* of solute (the *molar* entropy) will of course always increase as the solution becomes more dilute.

For gaseous substances, the volume and pressure are respectively direct and inverse measures of concentration. For an ideal gas that expands at a constant temperature (meaning that it absorbs heat from the surroundings to compensate for the work it does during the expansion), the increase in entropy is given by

[redacted]

Note: If the gas is allowed to cool during the expansion, the relation becomes more complicated and will best be discussed in a more advanced course.

Because the pressure of an ideal gas is *inversely proportional* to its volume, i.e.,

$$P = \frac{nRT}{V} \tag{2.5.1478}$$

we can easily alter Equation 2.5.985 to express the entropy change associated with a change in the pressure of an ideal gas:

[redacted]

Also the concentration $c = n/V$ for an ideal gas is *proportional* to pressure

$$P = cRT \tag{2.5.1479}$$

we can expressing the entropy change directly in concentrations, we have the similar relation

[redacted]

Although these equations strictly apply only to perfect gases and cannot be used at all for liquids and solids, it turns out that in a dilute solution, the solute can often be treated as a gas dispersed in the volume of the solution, so the last equation can actually give a fairly accurate value for the entropy of dilution of a solution. We will see later that this has important consequences in determining the equilibrium concentrations in a homogeneous reaction mixture.

The Relationship between Internal Energy and Entropy

Because the quantity of heat transferred (q_{rev}) is directly proportional to the absolute temperature of an object (T) ($q_{rev} \propto T$), the hotter the object, the greater the amount of heat transferred. Moreover, adding heat to a system increases the kinetic energy of the component atoms and molecules and hence their disorder ($\Delta S \propto q_{rev}$). Combining these relationships for any reversible process,

$$q_{\text{rev}} = T\Delta S \tag{2.5.1480}$$

and

[redacted]

Because the numerator (q_{rev}) is expressed in units of energy (joules), the units of ΔS are joules/kelvin (J/K). Recognizing that the work done in a reversible process at constant pressure is

$$w_{rev} = -P\Delta V, \tag{2.5.1481}$$

we can express Equation 1.1.1 as follows:

[redacted]

Thus the change in the internal energy of the system is related to the change in entropy, the absolute temperature, and the PV work done.

To illustrate the use of Equation 1.1.2 and Equation 1.1.5, we consider two reversible processes before turning to an irreversible process. When a sample of an ideal gas is allowed to expand reversibly at constant temperature, heat must be added to the gas during expansion to keep its T constant (Figure 2.5.5). The internal energy of the gas does not change because the temperature of the gas does not change; that is, ΔU = 0 and $q_{rev} = -w_{rev}$. During expansion, ΔV > 0, so the gas performs work on its surroundings:

$$w_{rev} = -P\Delta V < 0. \tag{2.5.1483}$$

According to Equation 1.1.5, this means that q_{rev} must increase during expansion; that is, the gas must absorb heat from the surroundings during expansion, and the surroundings must give up that same amount of heat. The entropy change of the *system* is therefore

$$\Delta S_{sys} = +\frac{q_{rev}}{T} \tag{2.5.1484}$$

and the entropy change of the *surroundings* is

$$\Delta S_{surr} = -\frac{q_{rev}}{T}. \tag{2.5.1485}$$

The corresponding change in entropy of the universe is then as follows:

[redacted]

Thus no change in ΔS_{univ} has occurred.

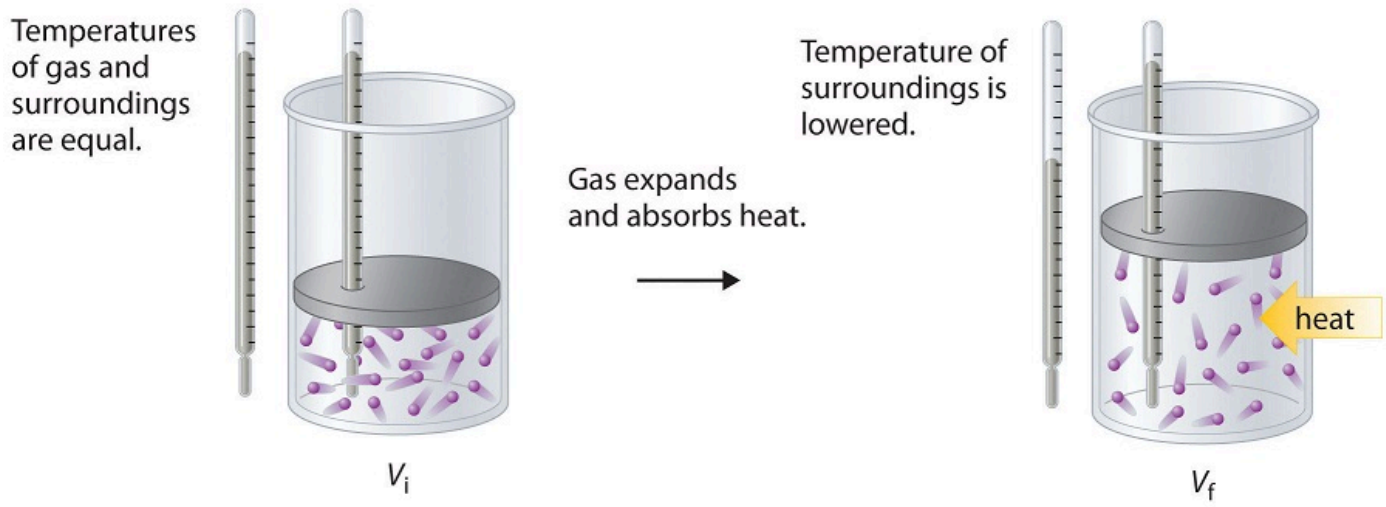


Figure 2.5.5: Expansion of Gas at Constant Temperature. (CC BY-SA-NC; Anonymous by request)

In the initial state (top), the temperatures of a gas and the surroundings are the same. During the reversible expansion of the gas, heat must be added to the gas to maintain a constant temperature. Thus the internal energy of the gas does not change, but work is performed on the surroundings. In the final state (bottom), the temperature of the surroundings is lower because the gas has absorbed heat from the surroundings during expansion.

Now consider the reversible melting of a sample of ice at 0°C and 1 atm. The enthalpy of fusion of ice is 6.01 kJ/mol, which means that 6.01 kJ of heat are absorbed reversibly from the surroundings when 1 mol of ice melts at 0°C, as illustrated in Figure 2.5.6 . The surroundings constitute a sample of low-density carbon foam that is thermally conductive, and the system is the ice cube that has been placed on it. The direction of heat flow along the resulting temperature gradient is indicated with an arrow. From Equation 1.1.2, we see that the entropy of fusion of ice can be written as follows:

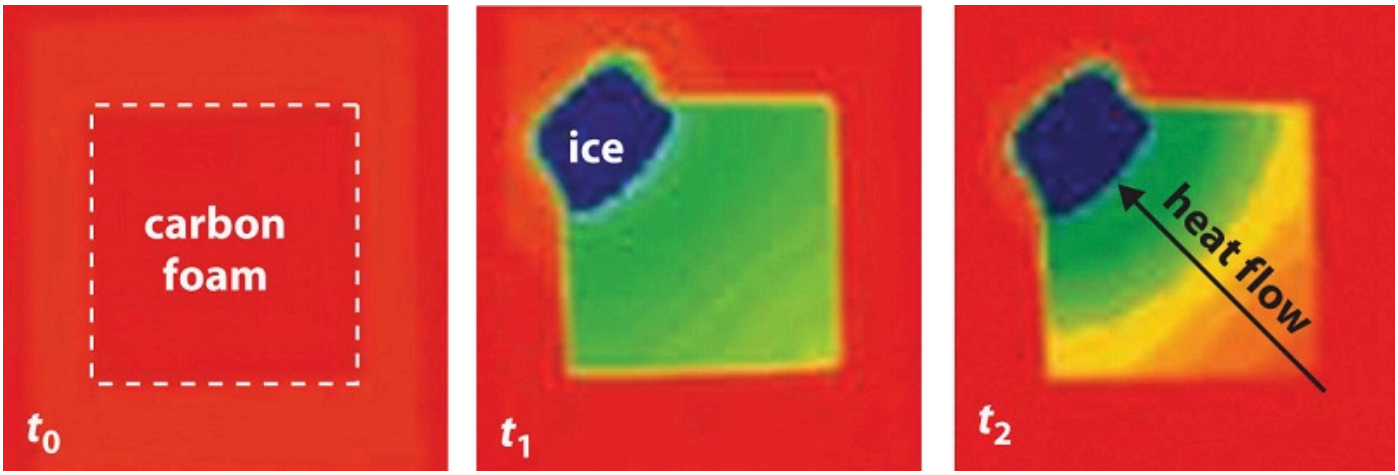


Figure 2.5.6: Thermograms Showing That Heat Is Absorbed from the Surroundings When Ice Melts at 0°C

By convention, a thermogram shows cold regions in blue, warm regions in red, and thermally intermediate regions in green. When an ice cube (the system, dark blue) is placed on the corner of a square sample of low-density carbon foam with very high thermal conductivity, the temperature of the foam is lowered (going from red to green). As the ice melts, a temperature gradient appears, ranging from warm to very cold. An arrow indicates the direction of heat flow from the surroundings (red and green) to the ice cube. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so the entropy of the universe does not change.

In this case,

$$\Delta S_{fus} = \frac{6.01\,kJ/mol}{273\,K} \tag{2.5.1488}$$

$$= 22.0\,J/(mol \bullet K) \tag{2.5.1489}$$

$$= \Delta S_{sys}. \tag{2.5.1490}$$

The amount of heat lost by the surroundings is the same as the amount gained by the ice, so

$$\Delta S_{surr} = \frac{q_{rev}}{T} \tag{2.5.1491}$$

$$= \frac{-6.01\,kJ/mol}{273\,K} \tag{2.5.1492}$$

$$= -22.0\,J/(mol \bullet K). \tag{2.5.1493}$$

Once again, we see that the entropy of the universe does not change:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \tag{2.5.1494}$$

$$= 22.0\,J/(mol \bullet K) - 22.0\,J/(mol \bullet K) \tag{2.5.1495}$$

$$= 0 \tag{2.5.1496}$$

In these two examples of reversible processes, the entropy of the universe is unchanged. This is true of all reversible processes and constitutes part of the second law of thermodynamics: the entropy of the universe remains constant in a reversible process, whereas the entropy of the universe increases in an irreversible (spontaneous) process.

The Second Law of Thermodynamics

The entropy of the universe **increases** during a spontaneous process. It also **increases** during an observable non-spontaneous process.

As an example of an irreversible process, consider the entropy changes that accompany the spontaneous and irreversible transfer of heat from a hot object to a cold one, as occurs when lava spewed from a volcano flows into cold ocean water. The cold substance, the water, gains heat ($q > 0$), so the change in the entropy of the water can be written as $\Delta S_{cold} = q/T_{cold}$. Similarly, the hot substance, the lava, loses heat ($q < 0$), so its entropy change can be written as $\Delta S_{hot} = -q/T_{hot}$, where T_{cold} and T_{hot} are the temperatures of the cold and hot substances, respectively. The total entropy change of the universe accompanying this process is therefore



The numerators on the right side of Equation 2.5.1009 are the same in magnitude but opposite in sign. Whether ΔS_{univ} is positive or negative depends on the relative magnitudes of the denominators. By definition, $T_{hot} > T_{cold}$, so $-q/T_{hot}$ must be less than q/T_{cold}, and ΔS_{univ} must be positive. As predicted by the second law of thermodynamics, the entropy of the universe increases during this irreversible process. Any process for which ΔS_{univ} is positive is, by definition, a spontaneous one that will occur as written. Conversely, any process for which ΔS_{univ} approaches zero will not occur spontaneously as written but will occur spontaneously in the reverse direction. We see, therefore, that heat is spontaneously transferred from a hot substance, the lava, to a cold substance, the ocean water. In fact, if the lava is hot enough (e.g., if it is molten), so much heat can be transferred that the water is converted to steam (Figure 2.5.7).



Figure 2.5.7: Spontaneous Transfer of Heat from a Hot Substance to a Cold Substance

When molten lava flows into cold ocean water, so much heat is spontaneously transferred to the water that steam is produced.

Example 2.5.1: Tin Pest

Tin has two allotropes with different structures. Gray tin (α-tin) has a structure similar to that of diamond, whereas white tin (β-tin) is denser, with a unit cell structure that is based on a rectangular prism. At temperatures greater than 13.2°C, white tin is the more stable phase, but below that temperature, it slowly converts reversibly to the less dense, powdery gray phase. This phenomenon was argued to plagued Napoleon's army during his ill-fated invasion of Russia in 1812: the buttons on his soldiers' uniforms were made of tin and disintegrated during the Russian winter, adversely affecting the soldiers' health (and morale). The conversion of white tin to gray tin is exothermic, with ΔH = –2.1 kJ/mol at 13.2°C.

a. What is ΔS for this process?
b. Which is the more highly ordered form of tin—white or gray?

Given: ΔH and temperature

Asked for: ΔS and relative degree of order

Strategy:

Use Equation 1.1.2 to calculate the change in entropy for the reversible phase transition. From the calculated value of ΔS, predict which allotrope has the more highly ordered structure.

Solution

a. We know from Equation 1.1.2 that the entropy change for any reversible process is the heat transferred (in joules) divided by the temperature at which the process occurs. Because the conversion occurs at constant pressure, and ΔH and ΔU are essentially equal for reactions that involve only solids, we can calculate the change in entropy for the reversible phase transition where q_{rev} = ΔH. Substituting the given values for ΔH and temperature in kelvins (in this case, T = 13.2°C = 286.4 K),

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{(-2.1\ \text{kJ/mol})(1000\ \text{J/kJ})}{286.4\ \text{K}} = -7.3\ \ \text{J/(mol}\cdot\text{K)}$$

b. The fact that $\Delta S < 0$ means that entropy decreases when white tin is converted to gray tin. Thus gray tin must be the more highly ordered structure.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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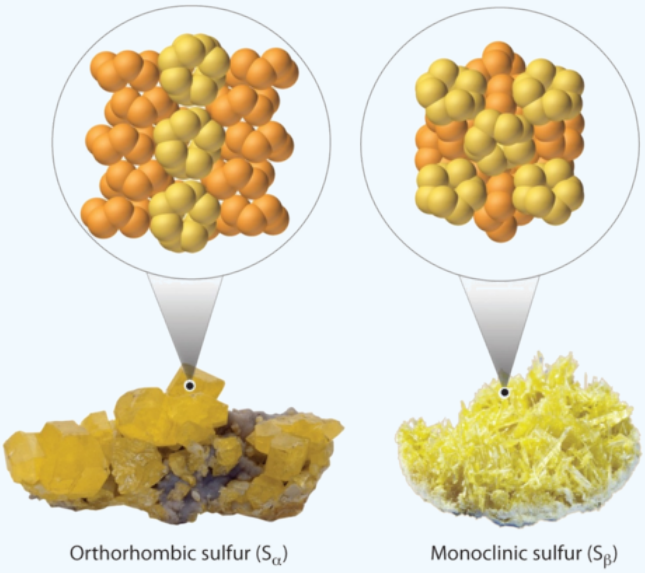
https://www.youtube.com/embed/sXB83Heh3_c?vq=hd1080

Video 2.5.1: Time lapse tin pest reaction. Beta tin to alpha tin transformation, time lapse video of sample maintained at -40 C. 20 shots per hour.

Note: Whether failing buttons were indeed a contributing factor in the failure of the invasion remains disputed; critics of the theory point out that the tin used would have been quite impure and thus more tolerant of low temperatures. Laboratory tests provide evidence that the time required for unalloyed tin to develop significant tin pest damage at lowered temperatures is about 18 months, which is more than twice the length of Napoleon's Russian campaign. It is clear though that some of the regiments employed in the campaign had tin buttons and that the temperature reached sufficiently low values (at least -40 °C) to facilitate tin pest.

Exercise 2.5.1: Sulfur

Elemental sulfur exists in two forms: an orthorhombic form (S_α), which is stable below 95.3°C, and a monoclinic form (S_β), which is stable above 95.3°C. The conversion of orthorhombic sulfur to monoclinic sulfur is endothermic, with $\Delta H = 0.401\ kJ/mol$ at 1 atm.



a. What is ΔS for this process?
b. Which is the more highly ordered form of sulfur—S_α or S_β?

Answer a

1.09 J/(mol•K)

Answer b

S_α

Summary

During a spontaneous process, the entropy of the universe increases.

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

A reversible process is one for which all intermediate states between extremes are *equilibrium states*; it can change direction at any time. In contrast, an irreversible process occurs in one direction only. The change in entropy of the system or the surroundings is the quantity of heat transferred divided by the temperature. The second law of thermodynamics states that in a reversible process, the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.

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2.6: Quantum States, Microstates, and Energy Spreading

Learning Objectives

- Explain how entropy is a measure of the degree of the spreading and sharing of thermal energy within a system.
- Explain why the entropy of a substance increases with its molecular weight and complexity and with temperature.
- Explain why entropy increases as the pressure or concentration becomes smaller.
- Explain why entropies of gases are much larger than those of condensed phases.

Entropy is a measure of the degree of spreading and sharing of thermal energy within a system. This “spreading and sharing” can be spreading of the thermal energy into a larger volume of *space* or its sharing amongst previously inaccessible microstates of the system. Entropy is an ***extensive* quantity**; that is, it is proportional to the quantity of matter in a system; thus 100 g of metallic copper has twice the entropy of 50 g at the same temperature. This makes sense because the larger piece of copper contains twice as many quantized energy levels able to contain the thermal energy.

Thermal energy is the portion of a molecule's energy that is proportional to its *temperature*, and thus relates to motion at the molecular scale. What kinds of molecular motions are possible? For monatomic molecules, there is only one: actual movement from one location to another, which we call *translation*. Since there are three directions in space, all molecules possess three modes of *translational motion*.

For polyatomic molecules, two additional kinds of motions are possible. One of these is *rotation*; a linear molecule such as CO_2 in which the atoms are all laid out along the x-axis can rotate along the y- and z-axes, while molecules having less symmetry can rotate about all three axes. Thus linear molecules possess two modes of rotational motion, while non-linear ones have three rotational modes. Finally, molecules consisting of two or more atoms can undergo internal *vibrations*. For freely moving molecules in a gas, the number of vibrational modes or patterns depends on both the number of atoms and the shape of the molecule, and it increases rapidly as the molecule becomes more complicated.

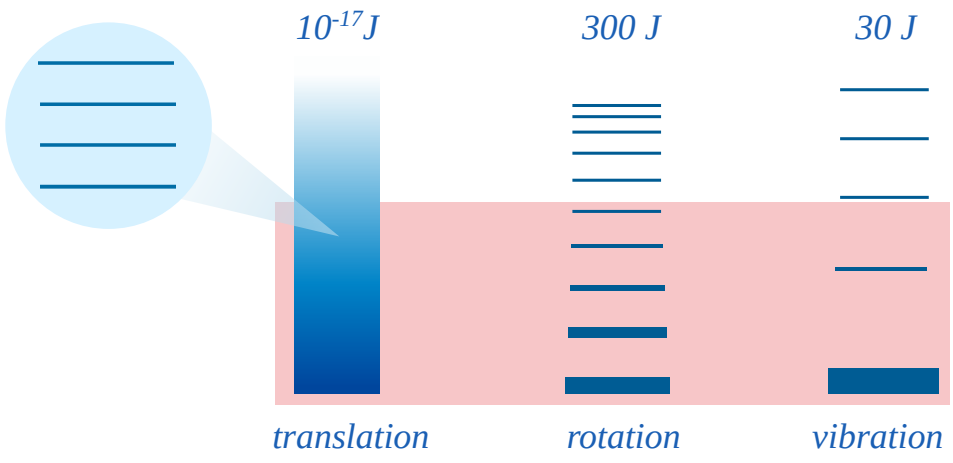
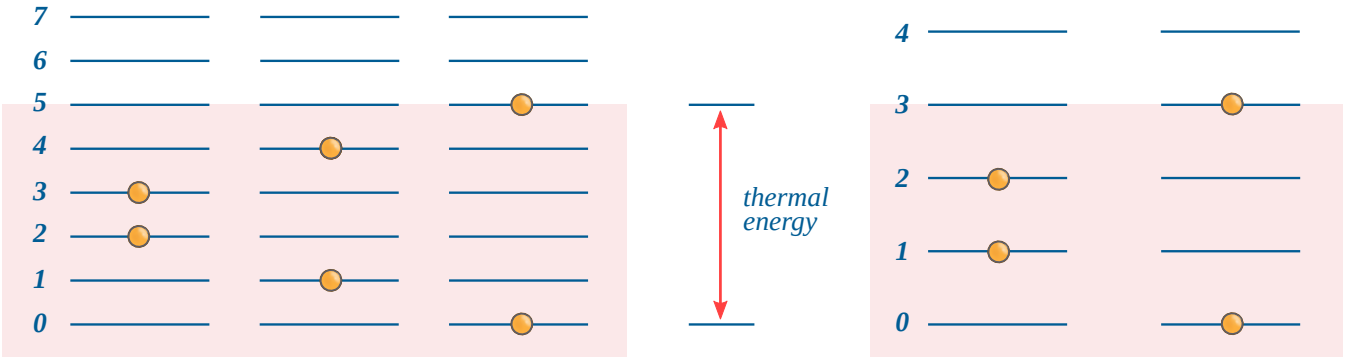


Figure 2.6.1: Relative Energy levels for translation (left), rotation (middle) and vibration (right). (CC BY-NC 4.0; Ümit Kaya based off of figure by Stephen Lower)

The relative populations of the quantized translational, rotational, and vibrational energy states of a typical diatomic molecule are depicted by the thickness of the lines in this schematic (not-to-scale!) diagram. The colored shading indicates the total thermal energy available at a given temperature. The numbers at the top show order-of-magnitude spacings between adjacent levels. It

is readily apparent that virtually all the thermal energy resides in translational states.

Notice the greatly different spacing of the three kinds of energy levels in Figure 2.6.1. This is extremely important because it determines the number of energy quanta that a molecule can accept, and, as Figure 2.6.2 demonstrates, the number of different ways this energy can be distributed amongst the molecules.



The quantity of energy indicated by the vertical arrow can be distributed in three ways in a collection of molecules whose allowed energy levels are spaced as shown here

In molecules with more widely-spaced energy levels there are fewer ways of distributing the same total energy

Figure 2.6.2: The more closely spaced the quantized energy states of a molecule, the greater will be the number of ways in which a given quantity of thermal energy can be shared amongst a collection of these molecules. (CC BY-NC 4.0; Ümit Kaya based off of figure by Stephen Lower)

The spacing of molecular energy states becomes closer as the mass and number of bonds in the molecule increases, so we can generally say that the more complex the molecule, the greater the density of its energy states.

At the atomic and molecular level, all energy is *quantized*; each particle possesses discrete states of kinetic energy and is able to accept thermal energy only in packets whose values correspond to the energies of one or more of these states. Polyatomic molecules can store energy in rotational and vibrational motions, and all molecules (even monatomic ones) will possess translational kinetic energy (thermal energy) at all temperatures above absolute zero. The energy difference between adjacent translational states is so minute that translational kinetic energy can be regarded as *continuous* (non-quantized) for most practical purposes.

The number of ways in which thermal energy can be distributed amongst the allowed states within a collection of molecules is easily calculated from simple statistics, but we will confine ourselves to an example here. Suppose that we have a system consisting of three molecules and three quanta of energy to share among them. We can give all the kinetic energy to any one molecule, leaving the others with none, we can give two units to one molecule and one unit to another, or we can share out the energy equally and give one unit to each molecule. All told, there are ten possible ways of distributing three units of energy among three identical molecules as shown here:

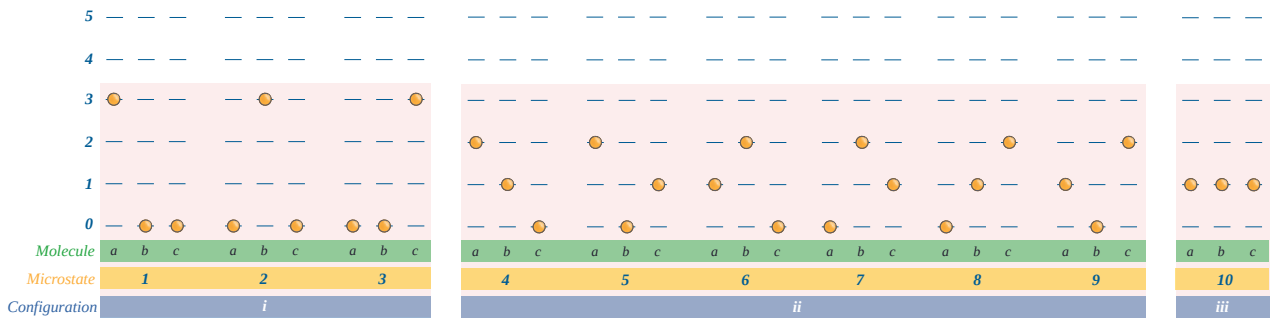


Figure 2.6.3. (CC BY-NC 4.0; Ümit Kaya based off of figure by Stephen Lower)

Each of these ten possibilities represents a distinct *microstate* that will describe the system at any instant in time. Those microstates that possess identical distributions of energy among the accessible quantum levels (and differ only in which particular molecules occupy the levels) are known as **configurations**. Because all microstates are equally probable, the probability of any one configuration is proportional to the number of microstates that can produce it. Thus in the system shown above, the configuration labeled *ii* will be observed 60% of the time, while *iii* will occur only 10% of the time.

As the number of molecules and the number of quanta increases, the number of accessible microstates grows explosively; if 1000 quanta of energy are shared by 1000 molecules, the number of available microstates will be around 10^{600}— a number that greatly exceeds the number of atoms in the observable universe! The number of possible configurations (as defined above) also increases, but in such a way as to greatly reduce the probability of all but the most probable configurations. Thus for a sample of a gas large enough to be observable under normal conditions, **only a single configuration (energy distribution amongst the quantum states) need be considered**; even the second-most-probable configuration can be neglected.

The bottom line: any collection of molecules large enough in numbers to have chemical significance will have its thermal energy distributed over an unimaginably large number of microstates. The number of microstates increases exponentially as more energy states ("configurations" as defined above) become accessible owing to

- Addition of energy quanta (higher temperature),
- Increase in the number of molecules (resulting from dissociation, for example).
- the volume of the system increases (which decreases the spacing between energy states, allowing more of them to be populated at a given temperature.)

Spontaneous Process: Heat Death

Energy is *conserved*; if you lift a book off the table, and let it fall, the total amount of energy in the world remains unchanged. All you have done is transferred it from the form in which it was stored within the glucose in your body to your muscles, and then to the book (that is, you did work on the book by moving it up against the earth's gravitational field). After the book has fallen, this same quantity of energy exists as thermal energy (heat) in the book and table top.

What *has* changed, however, is the availability of this energy. Once the energy has spread into the huge number of thermal microstates in the warmed objects, the probability of its spontaneously (that is, by chance) becoming un-dispersed is essentially zero. Thus although the energy is still "there", it is forever beyond utilization or recovery. The profundity of this conclusion was recognized around 1900, when it was first described at the "heat death" of the world. This refers to the fact that every spontaneous process (essentially every change that occurs) is accompanied by the "dilution" of energy. The obvious implication is that all of the molecular-level kinetic energy will be spread out completely, and nothing more will ever happen.

Spontaneous Process: Gases Expansions

Everybody knows that a gas, if left to itself, will tend to expand and fill the volume within which it is confined completely and uniformly. What "drives" this expansion? At the simplest level it is clear that with more space available, random motions of the individual molecules will inevitably disperse them throughout the space. But as we mentioned above, the allowed energy states

that molecules can occupy are spaced more closely in a larger volume than in a smaller one. The larger the volume available to the gas, the greater the number of microstates its thermal energy can occupy. Since all such states within the thermally accessible range of energies are equally probable, the expansion of the gas can be viewed as a consequence of the tendency of thermal energy to be spread and shared as widely as possible. Once this has happened, the probability that this sharing of energy will reverse itself (that is, that the gas will spontaneously contract) is so minute as to be unthinkable.

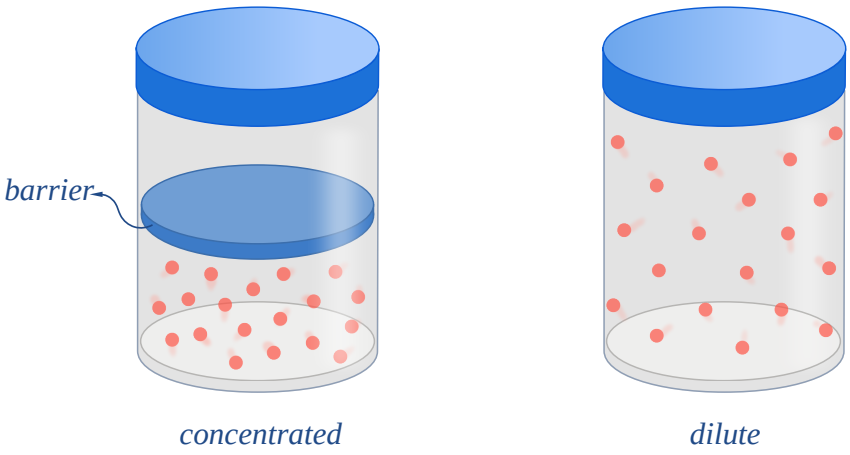


Figure 2.6.4: (CC BY-NC 4.0; Ümit Kaya based off of figure by Stephen Lower)

Imagine a gas initially confined to one half of a box (Figure 2.6.4). The barrier is then removed so that it can expand into the full volume of the container. We know that the entropy of the gas will increase as the thermal energy of its molecules spreads into the enlarged space. In terms of the spreading of thermal energy, Figure Figure 2.6.5 may be helpful. The tendency of a gas to expand is due to the more closely-spaced thermal energy states in the larger volume (2).

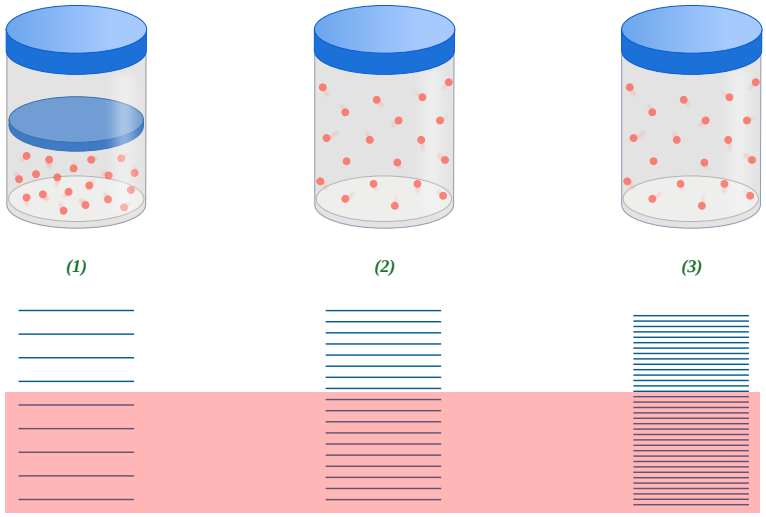


Figure 2.6.5: The pink shading represents the thermally-accessible range of microstates for a given temperature. (CC BY-NC 4.0; Ümit Kaya based off of figure by Stephen Lower)

Spontaneous Process: Mixing and dilution

Mixing and dilution really amount to the same thing, especially for ideal gases. Replace the pair of containers shown above with one containing two kinds of molecules in the separate sections (Figure 2.6.6). When we remove the barrier, the "red" and "blue" molecules will each expand into the space of the other. (Recall Dalton's Law that "each gas is a vacuum to the other gas"). However, notice that although each gas underwent an expansion, the overall process amounts to what we call "mixing".

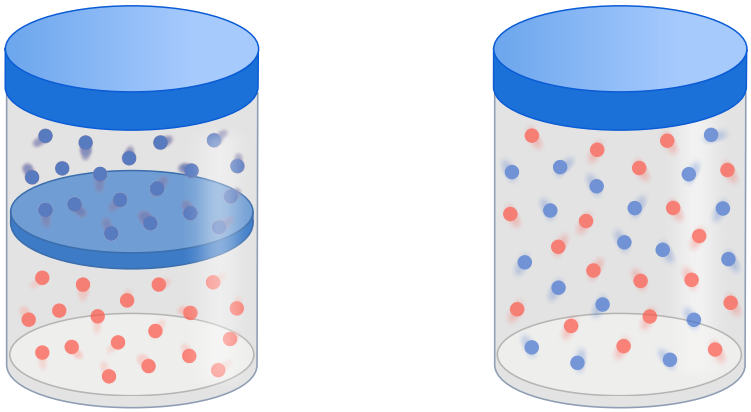


Figure 2.6.6: Mixing of a gas. (CC BY-NC 4.0; Ümit Kaya based off of figure by Stephen Lower)

What is true for gaseous molecules can, in principle, apply also to solute molecules dissolved in a solvent. But bear in mind that whereas the enthalpy associated with the expansion of a perfect gas is by definition zero, ΔH's of mixing of two liquids or of dissolving a solute in a solvent have finite values which may limit the miscibility of liquids or the solubility of a solute.

But what's really dramatic is that when just *one molecule* of a second gas is introduced into the container (3 in Figure 2.6.5), an unimaginably huge number of new configurations become possible, greatly increasing the number of microstates that are thermally accessible (as indicated by the pink shading above).

Spontaneous Process: Thermal Equilibrium

Just as gases spontaneously change their volumes from “smaller-to-larger”, the flow of heat from a warmer body to a cooler one always operates in the direction “warmer-to-cooler” because this allows thermal energy to populate a larger number of energy microstates as new ones are made available by bringing the cooler body into contact with the warmer one; in effect, the thermal energy becomes more “diluted”.

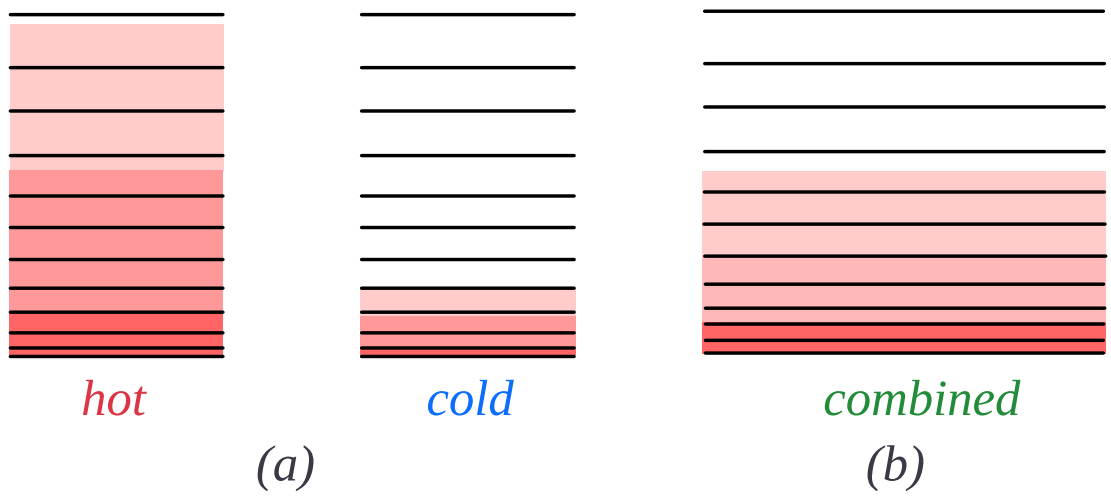


Figure 2.6.7: Part a of the figure is a schematic depiction of the thermal energy states in two separated identical bodies at different temperatures indicated by shading. (CC BY-NC 4.0; Ümit Kaya based off of figure by Stephen Lower)

When the bodies are brought into thermal contact (*b*), thermal energy flows from the higher occupied levels in the warmer object into the unoccupied levels of the cooler one until equal numbers are occupied in both bodies, bringing them to the same temperature. As you might expect, the increase in the amount of energy spreading and sharing is proportional to the amount of heat transferred *q*, but there is one other factor involved, and that is the *temperature* at which the transfer occurs. When a quantity of heat *q* passes into a system at temperature T, the degree of dilution of the thermal energy is given by



To understand why we have to divide by the temperature, consider the effect of very large and very small values of T in the denominator of Equation 2.6.1010. If the body receiving the heat is initially at a very low temperature, relatively few thermal energy states are initially occupied, so the amount of energy spreading into vacant states can be very great. Conversely, if the temperature is initially large, more thermal energy is already spread around within it, and absorption of the additional energy will have a relatively small effect on the degree of thermal disorder within the body.

Summary

Entropy is a measure of the degree of spreading and sharing of thermal energy within a system. This "spreading and sharing" can be spreading of the thermal energy into a larger volume of *space* or its sharing amongst previously inaccessible microstates of the system. The following box shows how this concept applies to a number of common processes.

Observations and Explanations in terms of Entropy changes

A deck of cards is shuffled, or 100 coins, initially heads up, are randomly tossed.

Source of Entropy Increase of System

> *This has nothing to do with entropy* because macro objects are unable to exchange thermal energy with the surroundings within the time scale of the process

Two identical blocks of copper, one at 20°C and the other at 40°C, are placed in contact.

Source of Entropy Increase of System

The cooler block contains more unoccupied microstates, so heat flows from the warmer block until equal numbers of microstates are populated in the two blocks.

A gas expands isothermally to twice its initial volume.

Source of Entropy Increase of System

A constant amount of thermal energy spreads over a larger volume of space

1 mole of water is heated by 1C°.

Source of Entropy Increase of System

The increased thermal energy makes additional microstates accessible. (The increase is by a factor of about $10^{20,000,000,000,000,000,000,000}$.)

Equal volumes of two gases are allowed to mix.

Source of Entropy Increase of System

The effect is the same as allowing each gas to expand to twice its volume; the thermal energy in each is now spread over a larger volume.

One mole of dihydrogen, H_2, is placed in a container and heated to 3000K.

Source of Entropy Increase of System

Some of the $\mathrm{H_2}$ dissociates to H atoms because at this temperature there are more thermally accessible microstates in the 2 moles of H atoms.

The above reaction mixture is cooled to 300 K.

Source of Entropy Increase of System

The composition shifts back to virtually all $\mathrm{H_2}$ because this molecule contains more thermally accessible microstates at low temperatures.

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2.7: The Third Law of Thermodynamics

Learning Objectives

- The *absolute entropy* of a pure substance at a given temperature is the sum of all the entropy it would acquire on warming from absolute zero (where $S = 0$) to the particular temperature.
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 2.7.1). The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion (ignoring quantum *zero point motion*).

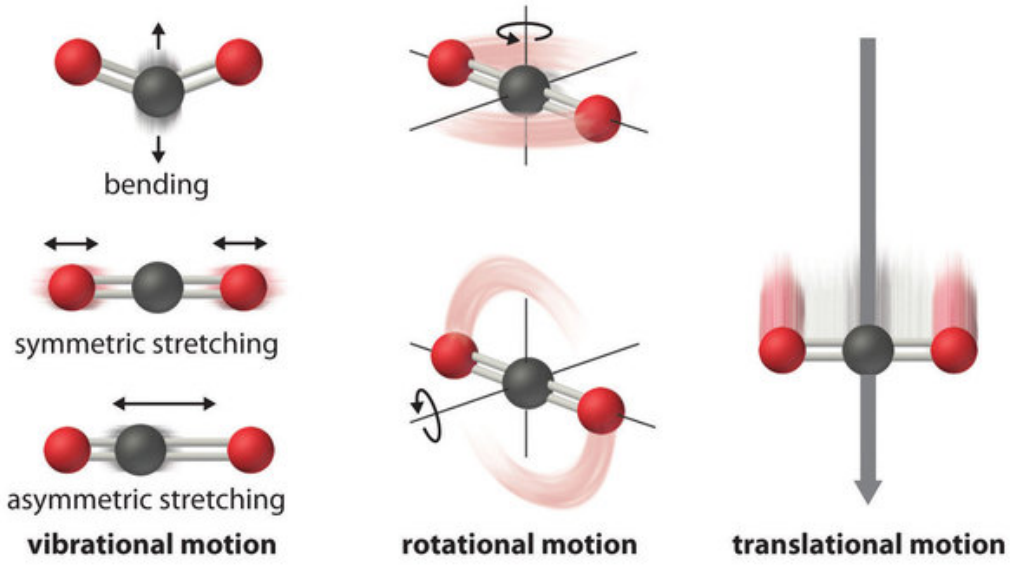


Figure 2.7.1: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion (classically; there will always be motion quantum mechanically) and have zero entropy. In practice, this is an unattainable ideal. (CC BY-SA-NC 3.0; Anonymous by request)

This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion (at least classically, quantum mechanics argues for constant motion) means there is but one possible location for each identical atom or molecule comprising the crystal ($\Omega = 1$). According to the Boltzmann equation, the entropy of this system is zero.

In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for the third law of thermodynamics: the entropy of any perfectly ordered, crystalline substance at absolute zero is zero.

Definition: Third Law of Thermodynamics

The entropy of a pure, perfect crystalline substance at 0 K is zero.

The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature. In this section, we examine two different ways to calculate ΔS for a reaction or a physical change. The first, based on the definition of absolute entropy provided by the third law of thermodynamics, uses tabulated values of absolute entropies of substances. The second, based on the fact that entropy is a state function, uses a thermodynamic cycle similar to those discussed previously.

Standard-State Entropies

One way of calculating ΔS for a reaction is to use tabulated values of the standard molar entropy (S^o), which is the entropy of 1 mol of a substance under standard pressure (1 bar). Often the standard molar entropy is given at 298 K and is often demarked as ΔS^o_{298}. The units of S^o are J/(mol•K). Unlike enthalpy or internal energy, it is possible to obtain absolute entropy values by measuring the entropy change that occurs between the reference point of 0 K (corresponding to $S = 0$) and 298 K (Tables T1 and T2).

As shown in Table 2.7.1, for substances with approximately the same molar mass and number of atoms, S^o values fall in the order

$$S^o(\text{gas}) \gg S^o(\text{liquid}) > S^o(\text{solid}). \tag{2.7.1498}$$

For instance, S^o for liquid water is 70.0 J/(mol•K), whereas S^o for water vapor is 188.8 J/(mol•K). Likewise, S^o is 260.7 J/(mol•K) for gaseous I_2 and 116.1 J/(mol•K) for solid I_2. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases (Figure 2.7.1). The correlation between physical state and absolute entropy is illustrated in Figure 2.7.2, which is a generalized plot of the entropy of a substance versus temperature.

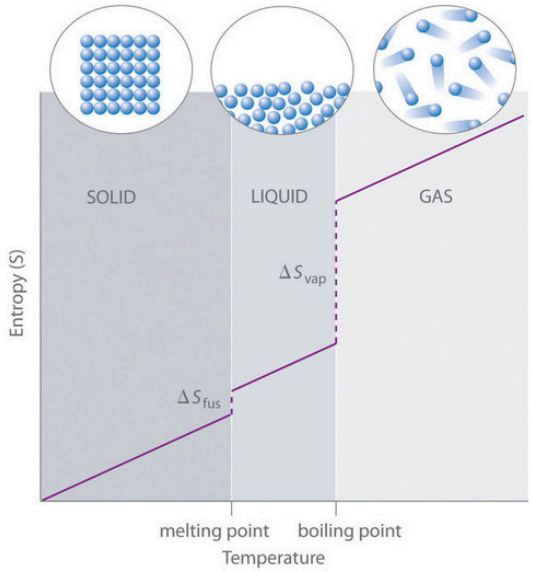


Figure 2.7.2: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (ΔS_{fus}). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas (ΔS_{vap}). (CC BY-SA-NC 3.0; anonymous).

The Third Law Lets us Calculate Absolute Entropies

The *absolute entropy* of a substance at any temperature above 0 K must be determined by calculating the increments of heat q required to bring the substance from 0 K to the temperature of interest, and then summing the ratios q/T. Two kinds of experimental measurements are needed:

1. The enthalpies associated with any **phase changes** the substance may undergo within the temperature range of interest. Melting of a solid and vaporization of a liquid correspond to sizeable increases in the number of microstates available to

accept thermal energy, so as these processes occur, energy will flow into a system, filling these new microstates to the extent required to maintain a constant temperature (the freezing or boiling point); these inflows of thermal energy correspond to the heats of fusion and vaporization. The entropy increase associated with transition at temperature T is

$$\frac{\Delta H_{fusion}}{T}. \tag{2.7.1499}$$

2. The **heat capacity** C of a phase expresses the quantity of heat required to change the temperature by a small amount ΔT, or more precisely, by an infinitesimal amount dT. Thus the entropy increase brought about by warming a substance over a range of temperatures that does not encompass a phase transition is given by the sum of the quantities $C\frac{dT}{T}$ for each increment of temperature dT. This is of course just the integral

[redacted]

Because the heat capacity is itself slightly temperature dependent, the most precise determinations of absolute entropies require that the functional dependence of C on T be used in the integral in Equation 2.7.1013, i.e.,:

[redacted]

When this is not known, one can take a series of heat capacity measurements over narrow temperature increments ΔT and measure the area under each section of the curve. The area under each section of the plot represents the entropy change associated with heating the substance through an interval ΔT. To this must be added the enthalpies of melting, vaporization, and of any solid-solid phase changes.

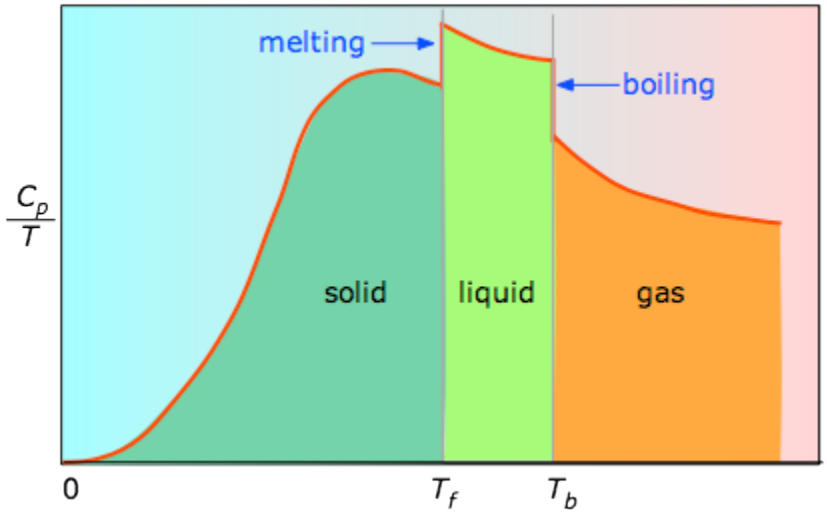


Figure 2.7.3: Heat capacity/temperature as a function of temperature. (CC BY 3.0; Stephan Lower)

Values of C_p for temperatures near zero are not measured directly, but can be estimated from quantum theory. The cumulative areas from 0 K to any given temperature (Figure 2.7.3) are then plotted as a function of T, and any phase-change entropies such as

$$S_{vap} = \frac{H_{vap}}{T_b} \tag{2.7.1500}$$

are added to obtain the absolute entropy at temperature T. As shown in Figure 2.7.2 above, the entropy of a substance increases with temperature, and it does so for two reasons:

- As the temperature rises, more microstates become accessible, allowing thermal energy to be more widely dispersed. This is reflected in the gradual increase of entropy with temperature.
- The molecules of solids, liquids, and gases have increasingly greater freedom to move around, facilitating the spreading and sharing of thermal energy. Phase changes are therefore accompanied by massive and discontinuous increase in the entropy.

Calculating ΔS_{sys}

We can make careful calorimetric measurements to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. Standard entropies are given the label S^o_{298} for values determined for one mole of substance at a pressure of 1 bar and a temperature of 298 K. The standard entropy change (ΔS^o) for any process may be computed from the standard entropies of its reactant and product species like the following:

[redacted]

Here, ν represents stoichiometric coefficients in the balanced equation representing the process. For example, ΔS^o for the following reaction at room temperature

[redacted]

is computed as the following:

[redacted]

Table 2.7.1 lists some standard entropies at 298.15 K. You can find additional standard entropies in Tables T1 and T2

Table 2.7.1: Standard Molar Entropy Values of Selected Substances at 25°C

Gases		Liquids		Solids	
Substance	S^o *[J/(mol•K)]*	*Substance*	S^o *[J/(mol•K)]*	*Substance*	S^o *[J/(mol•K)]*
He	126.2	H_2O	70.0	C (diamond)	2.4
H_2	130.7	CH_3OH	126.8	C (graphite)	5.7
Ne	146.3	Br_2	152.2	LiF	35.7
Ar	154.8	CH_3CH_2OH	160.7	SiO_2 (quartz)	41.5
Kr	164.1	C_6H_6	173.4	Ca	41.6
Xe	169.7	CH_3COCl	200.8	Na	51.3
H_2O	188.8	C_6H_{12} (cyclohexane)	204.4	MgF_2	57.2
N_2	191.6	C_8H_{18} (isooctane)	329.3	K	64.7
O_2	205.2			NaCl	72.1
CO_2	213.8			KCl	82.6
I_2	260.7			I_2	116.1

A closer examination of Table 2.7.1 also reveals that substances with similar molecular structures tend to have similar S^o values. Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond ($S^o = 2.4\ J/(mol \bullet K)$). In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher S^o (5.7 J/(mol•K)) due to more ~~disorder~~ (microstates) in the crystal. Soft crystalline substances and those with larger atoms tend to have higher entropies because of increased molecular motion and disorder. Similarly, the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the S^o values for $CH_3OH(l)$ and $CH_3CH_2OH(l)$. Finally, substances with strong hydrogen bonds have lower values of S^o, which reflects a more ordered structure.

> Entropy increases with softer, less rigid solids, solids that contain larger atoms, and solids with complex molecular structures.

To calculate ΔS^o for a chemical reaction from standard molar entropies, we use the familiar "products minus reactants" rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example 2.7.1 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

Example 2.7.1

Use the data in Table 2.7.1 to calculate ΔS^o for the reaction of liquid isooctane with $O_2(g)$ to give $CO_2(g)$ and $H_2O(g)$ at 298 K.

Given: standard molar entropies, reactants, and products

Asked for: ΔS°

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table 2.7.1 . Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain ΔS^o for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

$$C_8H_{18}(l) + \tfrac{25}{2}\,O_2(g) \longrightarrow 8\,CO_2(g) + 9\,H_2O(g)$$

We calculate ΔS^o for the reaction using the "products minus reactants" rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$\begin{aligned}\Delta S^o_{rxn} &= \sum mS^o(\text{products}) - \sum nS^o(\text{reactants})\\ &= [8S^o(CO_2) + 9S^o(H_2O)] - [S^o(C_8H_{18}) + \frac{25}{2}S^o(O_2)]\\ &= \{[8\text{ mol } CO_2 \times 213.8\text{ J/(mol}\cdot\text{K)}] + [9\text{ mol } H_2O \times 188.8\text{ J/(mol}\cdot\text{K)}]\}\\ &\quad - \left\{[1\text{ mol } C_8H_{18} \times 329.3\text{ J/(mol}\cdot\text{K)}] + \left[\frac{25}{2}\text{ mol } O_2 \times 205.2\text{ J/(mol}\cdot\text{K)}\right]\right\}\\ &= 515.3\text{ J/K}\end{aligned}$$

ΔS^o is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

Exercise 2.7.1

Use the data in Table 2.7.1 to calculate ΔS^o for the reaction of $H_2(g)$ with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}) at 298 K.

Answer

-361.1 J/K

Example 2.7.2: Determination of ΔS°

Calculate the standard entropy change for the following process at 298 K:

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

Solution

The value of the standard entropy change at room temperature, ΔS^o_{298}, is the difference between the standard entropy of the product, $H_2O(l)$, and the standard entropy of the reactant, $H_2O(g)$.

$$\begin{aligned}\Delta S^o_{298} &= S^o_{298}(\mathrm{H_2O\,(l)}) - S^o_{298}(\mathrm{H_2O\,(g)}) \\ &= (70.0\ J\,mol^{-1}K^{-1}) - (188.8\ Jmol^{-1}K^{-1}) \\ &= -118.8\ J\,mol^{-1}K^{-1}\end{aligned}$$

The value for ΔS^o_{298} is negative, as expected for this phase transition (condensation), which the previous section discussed.

Exercise 2.7.2

Calculate the standard entropy change for the following process at 298 K:

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

Answer

$-120.6\ \mathrm{J\ mol^{-1}\ K^{-1}}$

Example 2.7.3: Determination of ΔS°

Calculate the standard entropy change for the combustion of methanol, CH_3OH at 298 K:

$$2\,\mathrm{CH_3OH}(l) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(l)$$

Solution

The value of the standard entropy change is equal to the difference between the standard entropies of the products and the entropies of the reactants scaled by their stoichiometric coefficients. The standard entropy of formations are found in Table 2.7.1.

$$\begin{aligned}\Delta S^o &= \Delta S^o_{298} \\ &= \sum \nu S^o_{298}(\text{products}) - \sum \nu S^o_{298}(\text{reactants}) \\ &= 2S^o_{298}(\mathrm{CO_2}(g)) + 4S^o_{298}(\mathrm{H_2O}(l))] - [2S^o_{298}(\mathrm{CH_3OH}(l)) + 3S^o_{298}(\mathrm{O_2}(g))] \\ &= [(2 \times 213.8) + (4 \times 70.0)] - [(2 \times 126.8) + (3 \times 205.03)] \\ &= -161.6\ J/mol \cdot K\end{aligned}$$

Exercise 2.7.3

Calculate the standard entropy change for the following reaction at 298 K:

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

Answer

24.7 J/mol•K

Summary

Energy values, as you know, are all relative, and must be defined on a scale that is completely arbitrary; there is no such thing as the absolute energy of a substance, so we can arbitrarily define the enthalpy or internal energy of an element in its most stable form at 298 K and 1 atm pressure as zero. The same is *not* true of the entropy; since entropy is a measure of the "dilution" of thermal energy, it follows that the less thermal energy available to spread through a system (that is, the lower the temperature), the smaller will be its entropy. In other words, as the absolute temperature of a substance approaches zero, so does its entropy. This principle is the basis of the *Third law of thermodynamic*s, which states that the entropy of a perfectly-ordered solid at 0 K is zero.

In practice, chemists determine the absolute entropy of a substance by measuring the molar heat capacity (C_p) as a function of temperature and then plotting the quantity C_p/T versus T. The area under the curve between 0 K and any temperature T is the absolute entropy of the substance at T. In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only relative terms, not absolute terms.

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe, $S_{univ} > 0$. If $\Delta S_{univ} < 0$, the process is nonspontaneous, and if $\Delta S_{univ} = 0$, the system is at equilibrium. The third law of thermodynamics establishes the zero for entropy as that of a perfect, pure crystalline solid at 0 K. With only one possible microstate, the entropy is zero. We may compute the standard entropy change for a process by using standard entropy values for the reactants and products involved in the process.

Contributors and Attributions

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- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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2.8: Gibbs Energy

Learning Objectives

- To understand the relationship between Gibbs free energy and work.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for **both a system and its surroundings**. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient and is provided by a new state function: the Gibbs free energy.

Gibbs Energy and Spontaneity

The Gibbs energy (also known as the *Gibbs function*) is defined as

[redacted]

in which S refers to the entropy of the *system*. Since H, T and S are all state functions, so is G. Thus for any change in state, we can expand Equation 2.8.1019 to

[redacted]

How does this simple equation relate to the entropy change of the universe ΔS_{univ} that we know is the sole criterion for spontaneous change from the second law of thermodynamics? Starting with the definition

[redacted]

we would first like to get rid of ΔS_{surr}. How can a chemical reaction (a change in the *system*) affect the entropy of the *surroundings*? Because most reactions are either exothermic or endothermic, they are accompanied by heat q_p across the system boundary (we are considering constant pressure processes). The enthalpy change of the reaction ΔH_{sys} is the "flow" of heat into the system from the surroundings under constant pressure, so the heat "withdrawn" from the surroundings will be $-q_p$.

From the thermodynamic definition of entropy, the change of the entropy of the surroundings will be

$$\Delta S_{surr} = -\frac{q_p}{T} = -\frac{\Delta H_{sys}}{T}. \tag{2.8.1501}$$

We can therefore rewrite Equation 2.8.1021 as

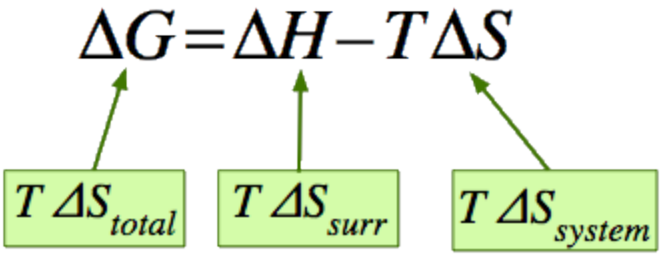
[redacted]

Multiplying through by $-T$, we obtain

[redacted]

which expresses the entropy change of the universe in terms of thermodynamic properties of the *system* exclusively.

If $-T\Delta S_{univ}$ is denoted by ΔG, then we have Equation 2.8.1020 which defines the *Gibbs energy* change for the process.



The criterion for predicting spontaneity is based on (ΔG), the change in G, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as G. At constant temperature and pressure,

[redacted]

where all thermodynamic quantities are those of the system. Recall that at constant pressure, $\Delta H = q$, whether a process is reversible or irreversible, and

$$T\Delta S = q_{rev}. \tag{2.8.1502}$$

Using these expressions, we can reduce Equation 1.1.2 to

$$\Delta G = q - q_{rev}. \tag{2.8.1503}$$

Thus ΔG is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, $q = q_{rev}$ and $\Delta G = 0$. As we shall soon see, if ΔG is zero, the system is at equilibrium, and there will be no net change.

What about processes for which $\Delta G \neq 0$? To understand how the sign of ΔG for a system determines the direction in which change is spontaneous, we can rewrite the relationship between ΔS and q_{rev}, discussed earlier.

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

with the definition of ΔH in terms of q_{rev}

$$q_{rev} = \Delta H$$

to obtain

[redacted]

Thus the entropy change of the surroundings is related to the enthalpy change of the system. We have stated that for a spontaneous reaction, $\Delta S_{univ} > 0$, so substituting we obtain

$$\begin{aligned} \Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \\ &= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \end{aligned}$$

Multiplying both sides of the inequality by $-T$ reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0 \tag{2.8.1504}$$

which is equal to ΔG (Equation 1.1.2). We can therefore see that for a spontaneous process, $\Delta G_{sys} < 0$.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 1.1.2 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H \ll 0$) that increase the entropy of a system ($\Delta S_{sys} \gg 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer.

Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995. For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G < 0$, the process occurs spontaneously.
- If $\Delta G = 0$, the system is at equilibrium.
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor.

Example 2.8.1: Vaporizing Water

At Room Temperature (100 °C)

If the conversion of liquid water to water vapor is carried out at 1 atm and the normal boiling point of 100.00 °C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol of water, $\Delta H = 40,657; J$, so the process is highly endothermic. From the definition of ΔS (Equation 1.1.5), we know that for 1 mol of water,

$$\begin{aligned}\Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} \\ &= \frac{40{,}657\ \text{J}}{373.15\ \text{K}} \\ &= 108.96\ \text{J/K}\end{aligned}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\begin{aligned}\Delta G_{100^\circ\text{C}} &= \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} \\ &= 40{,}657\ \text{J} - [(373.15\ \text{K})(108.96\ \text{J/K})] \\ &= 0\ \text{J}\end{aligned}$$

The energy required for vaporization offsets the increase in entropy of the system. Thus $\Delta G = 0$, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Above Room Temperature (110 °C)

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\begin{aligned}\Delta G_{110^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(383.15\ \text{K})(108.96\ \text{J/K})] \\ &= -1{,}091\ \text{J}\end{aligned}$$

Since $\Delta G < 0$, the vaporization of water is predicted to occur spontaneously and irreversibly at 110 °C.

Below Room Temperature (90 °C)

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\begin{aligned}\Delta G_{90^\circ C} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(363.15\ \text{K})(108.96\ \text{J/K})] \\ &= 1{,}088\ \text{J}\end{aligned}$$

Since $\Delta G > 0$, water does not spontaneously convert to water vapor at 90 °C. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110^\circ C} = 1090\ \text{J} = -\Delta G_{90^\circ C}$, as we would predict.

Equilibrium Temperature

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 1.1.2), setting $\Delta G = 0$, and solving for T,

$$\begin{aligned}0 &= 40,657\,J - T(108.96\,J/K) \\ T &= 373.15\,K\end{aligned}$$

Thus $\Delta G = 0$ at $T = 373.15\ K$ and $1\ atm$, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water.

At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 2.8.1 shows how the ΔH and $T\Delta S$ terms vary with temperature for the vaporization of water. When the two lines cross, $\Delta G = 0$, and $\Delta H = T\Delta S$.

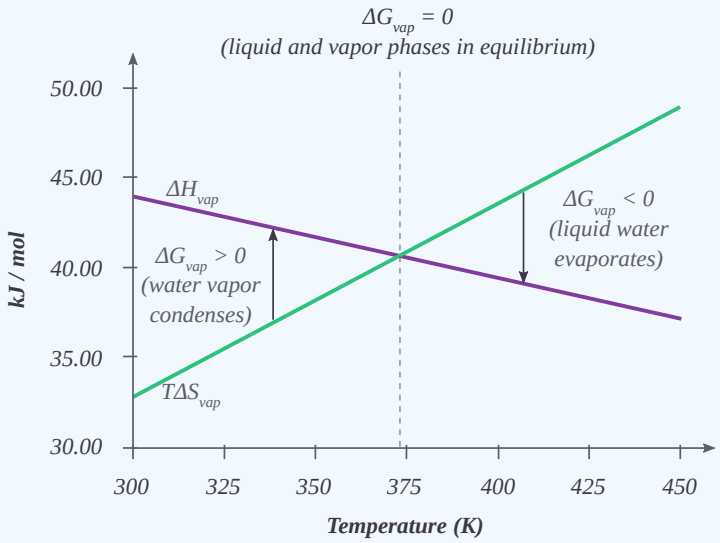


Figure 2.8.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH – TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the $T\Delta S$ term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than $T\Delta S$, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid. (CC BY-NC; Ümit Kaya)

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy ($\Delta H > 0$), which converts the albumin to a highly disordered structure in which the molecules aggregate as a disorganized solid ($\Delta S > 0$). At temperatures greater than 373 K, the $T\Delta S$ term dominates, and $\Delta G < 0$, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.

Figure 2.8.1

ΔH	ΔS	$-T\Delta S$	ΔG
- (exothermic)	+ (products more disordered)	- (favors spontaneity)	- (spontaneous at all T)
- (exothermic)	- (products less disordered)	+ (opposes spontaneity)	- (spontaneous) at low T + (non-spontaneous) at high T **"Enthalpically-driven process"**
+ (endothermic)	+ (products more disordered)	- (favors spontaneity)	+ (non-spontaneous) at low T - (spontaneous) at high T **"Entropically-driven process"**
+ (endothermic)	- (products less disordered)	+ (opposes spontaneity)	+ (non-spontaneous at all T)

Enthalpically vs. Entropically Driving Reactions

Some textbooks and teachers say that the free energy, and thus the spontaneity of a reaction, depends on both the enthalpy and entropy changes of a reaction, and they sometimes even refer to reactions as "energy driven" or "entropy driven" depending on whether ΔH or the $T\Delta S$ term dominates. This is technically correct, but misleading because it disguises the important fact that ΔS_{total}, which this equation expresses in an indirect way, is the *only* criterion of spontaneous change.

Consider the following possible states for two different types of molecules with some attractive force:

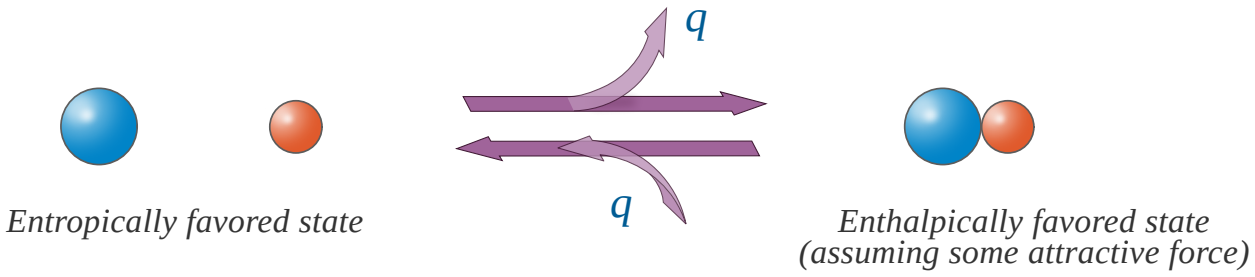


Figure 2.8.2: An enthalpic favored reaction. (CC BY-NC; Ümit Kaya)

There would appear to be greater entropy on the left (state 1) than on the right (state 2). Thus the entropic change for the reaction as written (i.e. going to the right) would be (-) in magnitude, and the energetic contribution to the free energy change would be (+) (i.e. unfavorable) for the reaction as written.

In going to the right, there is an attractive force and the molecules adjacent to each other is a lower energy state (heat energy, q , is liberated). To go to the left, we have to overcome this attractive force (input heat energy) and the left direction is unfavorable with regard to heat energy q. The change in enthalpy is (-) in going to the right (q released), and this enthalpy change is negative (-) in going to the right (and (+) in going to the left). This reaction as written, is therefore, *enthalpically favorable* and *entropically unfavorable*. Hence, It is *enthalpically driven*.

From Table 2.8.1, it would appear that we might be able to get the reaction to go to the right at low temperatures (lower temperature would minimize the energetic contribution of the entropic change). Looking at the same process from an opposite direction:

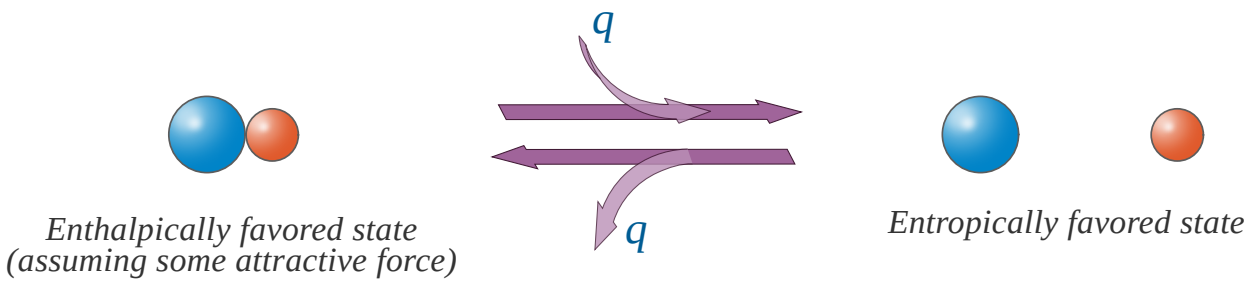


Figure 2.8.3: An entropically favored reaction. (CC BY-NC; Ümit Kaya)

This reaction as written, is *entropically favorable*, and *enthalpically unfavorable;* it is *entropically driven*. From Table 2.8.1, it would appear that we might be able to get the reaction to go to the right at high temperatures (high temperature would increase the energetic contribution of the entropic change).

The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in Gibbs energy is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure):

$$\Delta G = w_{max}. \tag{2.8.1505}$$

To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 1.1.2. We can rearrange this equation as follows:

[redacted]

This equation tells us that when energy is released during an exothermic process ($\Delta H < 0$), such as during the combustion of a fuel, some of that energy can be used to do work ($\Delta G < 0$), while some is used to increase the entropy of the universe ($T\Delta S > 0$). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 2.8.2, the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table 2.8.2: Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60

Device	Energy Conversion	Approximate Efficiency (%)
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 2.5.998:

[redacted]

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG^o depends on the relative magnitudes of the ΔH° and TΔS° terms. It is important to recognize that a positive value of ΔG^o for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

> A positive ΔG^o means that the equilibrium constant is less than 1.

Example 2.8.1

Calculate the standard free-energy change (ΔG°) at 25°C for the reaction

$$\mathrm{H_2\,(g) + O_2\,(g) \rightleftharpoons H_2O_2\,(l)}$$

At 25°C, the standard enthalpy change (ΔH°) is –187.78 kJ/mol, and the absolute entropies of the products and reactants are:

- S°(H_2O_2) = 109.6 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Is the reaction spontaneous as written?

Given: balanced chemical equation, ΔH° and S° for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A. Calculate ΔS° from the absolute molar entropy values given.
B. Use Equation 2.5.998, the calculated value of ΔS°, and other data given to calculate ΔG^o for the reaction.
C. Use the value of ΔG^o to determine whether the reaction is spontaneous as written.

Solution

A To calculate ΔG^o for the reaction, we need to know ΔH°, ΔS°, and T. We are given ΔH°, and we know that T = 298.15 K. We can calculate ΔS° from the absolute molar entropy values provided using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ &= S^\circ(\mathrm{H_2O_2}) - [S^\circ(\mathrm{O_2}) + S^\circ(\mathrm{H_2})] \\ &= [1\ \text{mol}\ \mathrm{H_2O_2} \times 109.6\ \mathrm{J/(mol \cdot K)}] \\ &\quad - \{[1\ \text{mol}\ \mathrm{H_2} \times 130.7\ \mathrm{J/(mol \cdot K)}] + [1\ \text{mol}\ \mathrm{O_2} \times 205.2\ \mathrm{J/(mol \cdot K)}]\} \\ &= -226.3\ \mathrm{J/K\ (per\ mole\ of\ H_2O_2)}\end{aligned}$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, ΔS° is very negative for this reaction.

B Substituting the appropriate quantities into Equation 2.5.998,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -187.78\ \mathrm{kJ/mol} - (298.15\ \mathrm{K})[-226.3\ \mathrm{J/(mol \cdot K)} \times 1\ \mathrm{kJ/1000\ J}] \\ &= -187.78\ \mathrm{kJ/mol} + 67.47\ \mathrm{kJ/mol} \\ &= -120.31\ \mathrm{kJ/mol}\end{aligned}$$

The negative value of ΔG^o indicates that the reaction is spontaneous as written. Because ΔS° and ΔH° for this reaction have the same sign, the sign of ΔG^o depends on the relative magnitudes of the ΔH° and TΔS° terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable ΔS° term and for the energy needed to break bonds in the reactants.

Exercise 2.8.1

Calculate the standard free-energy change (ΔG°) at 25°C for the reaction

$$2\,\mathrm{H_2\,(g)} + \mathrm{N_2\,(g)} \rightleftharpoons \mathrm{N_2H_4\,(l)}.$$

At 25°C, the standard enthalpy change (ΔH°) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are S°(N_2H_4) = 121.2 J/(mol•K), S°(N_2) = 191.6 J/(mol•K), and S°(H_2) = 130.7 J/(mol•K). Is the reaction spontaneous as written?

Answer

149.5 kJ/mol; no

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG^o for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation (ΔG°_f)of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $\Delta G^\circ_f = 0$. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation (ΔH°_f) and the standard entropy of formation (ΔS°_f) using the definition of free energy:

[redacted]

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar “products minus reactants” rule:

[redacted]

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG^o indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

"Products minus Reactants" Rule

The ΔG^o of a reaction can be calculated from tabulated ΔG^o_f values (Table T1) using the “products minus reactants” rule.

Example 2.8.2

Calculate ΔG^o for the reaction of isooctane with oxygen gas to give carbon dioxide and water. Use the following data:

- $\Delta G°_f$(isooctane) = –353.2 kJ/mol,
- $\Delta G°_f(CO_2)$ = –394.4 kJ/mol, and
- $\Delta G°_f(H_2O)$ = –237.1 kJ/mol.

Is the reaction spontaneous as written?

Given: balanced chemical equation and values of $\Delta G°_f$ for isooctane, CO_2, and H_2O

Asked for: spontaneity of reaction as written

Strategy:

Use the “products minus reactants” rule to obtain ΔG°_{rxn}, remembering that $\Delta G°_f$ for an element in its standard state is zero. From the calculated value, determine whether the reaction is spontaneous as written.

Solution

The balanced chemical equation for the reaction is as follows:

$$\mathrm{C_8H_{18}\,(l)} + \tfrac{25}{2}\,\mathrm{O_2\,(g)} \longrightarrow 8\,\mathrm{CO_2\,(g)} + 9\,\mathrm{H_2O\,(l)}$$

We are given ΔG°_f values for all the products and reactants except O_2(g). Because oxygen gas is an element in its standard state, $\Delta G^\circ_f\,(O_2)$ is zero. Using the “products minus reactants” rule,

$$\begin{aligned}\Delta G^\circ &= [8\Delta G^\circ_f(\mathrm{CO_2}) + 9\Delta G^\circ_f(\mathrm{H_2O})] - \left[1\Delta G^\circ_f(\mathrm{C_8H_{18}}) + \frac{25}{2}\Delta G^\circ_f(\mathrm{O_2})\right] \\ &= [(8\text{ mol})(-394.4\text{ kJ/mol}) + (9\text{ mol})(-237.1\text{ kJ/mol})] \\ &\quad - \left[(1\text{ mol})(-353.2\text{ kJ/mol}) + \left(\frac{25}{2}\text{ mol}\right)(0\text{ kJ/mol})\right] \\ &= -4935.9\text{ kJ (per mol of } \mathrm{C_8H_{18}})\end{aligned}$$

Because ΔG^o is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG^o is largely determined by the ΔG°_f of the stable products: water and carbon dioxide.

Exercise 2.8.2

Calculate ΔG^o for the reaction of benzene with hydrogen gas to give cyclohexane using the following data

- ΔG°_f(benzene) = 124.5 kJ/mol
- ΔG°_f (cyclohexane) = 217.3 kJ/mol.

Is the reaction spontaneous as written?

Answer

92.8 kJ; no

Calculated values of ΔG^o are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of ΔG^o may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from ΔG°. If the ΔH and TΔS terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG^o at various temperatures, as long as no phase change occurs over the temperature range being considered.

In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Example 2.8.3

Calculate (a) ΔG^o and (b) $\Delta G_{300°C}$ for the reaction $N_2(g)+3H_2(g)⇌2NH_3(g)$, assuming that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

- $S°(N_2)$ = 191.6 J/(mol•K),
- $S°(H_2)$ = 130.7 J/(mol•K),
- $S°(NH_3)$ = 192.8 J/(mol•K), and
- ΔH°_f (NH_3) = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, S° values, and ΔH°_f for NH_3

Asked for: ΔG^o and ΔG at 300°C

Strategy:

A. Convert each temperature to kelvins. Then calculate ΔS° for the reaction. Calculate ΔH° for the reaction, recalling that ΔH°_f for any element in its standard state is zero.
B. Substitute the appropriate values into Equation 2.5.998 to obtain ΔG^o for the reaction.

C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation 1.1.2 to obtain ΔG for the reaction at 300°C.

Solution

A To calculate ΔG^o for the reaction using Equation 2.5.998, we must know the temperature as well as the values of ΔS° and ΔH°. At standard conditions, the temperature is 25°C, or 298 K. We can calculate ΔS° for the reaction from the absolute molar entropy values given for the reactants and the products using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= 2S^\circ(\text{NH}_3) - [S^\circ(\text{N}_2) + 3S^\circ(\text{H}_2)] \\ &= [2 \text{ mol NH}_3 \times 192.8 \text{ J/(mol} \cdot \text{K)}] \\ &- \{[1 \text{ mol N}_2 \times 191.6 \text{ J/(mol} \cdot \text{K)}] + [3 \text{ mol H}_2 \times 130.7 \text{ J/(mol} \cdot \text{K)}]\} \\ &= -198.1 \text{ J/K (per mole of N}_2\text{)}\end{aligned}$$

We can also calculate ΔH° for the reaction using the "products minus reactants" rule. The value of ΔH°_f (NH_3) is given, and ΔH°_f is zero for both N_2 and H_2:

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= 2\Delta H^\circ_f(\text{NH}_3) - [\Delta H^\circ_f(\text{N}_2) + 3\Delta H^\circ_f(\text{H}_2)] \\ &= [2 \times (-45.9 \text{ kJ/mol})] - [(1 \times 0 \text{ kJ/mol}) + (3 \times 0 \text{ kJ/mol})] \\ &= -91.8 \text{ kJ(per mole of N}_2\text{)}\end{aligned}$$

B Inserting the appropriate values into Equation 2.5.998

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= \Delta H^\circ - T\Delta S^\circ \\ &= (-91.8 \text{ kJ}) - (298 \text{ K})(-198.1 \text{ J/K})(1 \text{ kJ}/1000 \text{ J}) \\ &= -32.7 \text{ kJ (per mole of N}_2\text{)}\end{aligned}$$

C To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300°C}$ = H° and $\Delta S_{300°C}$ = ΔS°) and insert the appropriate temperature (573 K) into Equation 1.1.2:

$$\begin{aligned}\Delta G_{300^\circ\text{C}} &= \Delta H_{300^\circ\text{C}} - (573 \text{ K})(\Delta S_{300^\circ\text{C}}) \\ &= \Delta H^\circ - (573 \text{ K})\Delta S^\circ \\ &= (-91.8 \text{ kJ}) - (573 \text{ K})(-198.1 \text{ J/K})(1 \text{ kJ}/1000 \text{ J}) \\ &= 21.7 \text{ kJ (per mole of N}_2\text{)}\end{aligned}$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is thermodynamically spontaneous, but in practice, it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more rapidly also changes the thermodynamics by causing the –TΔS° term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its K_{eq} is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

Exercise 2.8.3

Calculate

a. ΔG° and

b. $\Delta G_{750°C}$

for the following reaction

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

which is important in the formation of urban smog. Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

- S°(NO) = 210.8 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K),
- S°(NO_2) = 240.1 J/(mol•K),
- ΔH°_f(NO_2) = 33.2 kJ/mol, and
- ΔH°_f (NO) = 91.3 kJ/mol.

Answer a

–72.5 kJ/mol of O_2

Answer b

33.8 kJ/mol of O_2

The effect of temperature on the spontaneity of a reaction, which is an important factor in the design of an experiment or an industrial process, depends on the sign and magnitude of both ΔH° and ΔS°. The temperature at which a given reaction is at equilibrium can be calculated by setting ΔG^o = 0 in Equation 2.5.998, as illustrated in Example 2.8.4.

Example 2.8.4

As you saw in Example 2.8.3, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which ΔH° and ΔS° are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 2.8.3 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

Given: ΔH° and ΔS°

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set ΔG^o equal to zero in Equation 2.5.998 and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution

In Example 2.8.3, we calculated that ΔH° is –91.8 kJ/mol of N_2 and ΔS° is –198.1 J/K per mole of N_2, corresponding to ΔG^o = –32.7 kJ/mol of N_2 at 25°C. Thus the reaction is indeed spontaneous at low temperatures, as expected based on the signs of ΔH° and ΔS°. The temperature at which the reaction becomes nonspontaneous is found by setting ΔG^o equal to zero and rearranging Equation 2.5.998 to solve for T:

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

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

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{-198.1\ \text{J/K}} = 463\ \text{K}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

Exercise 2.8.4

As you found in the exercise in Example 2.8.3, ΔH° and ΔS° are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

Answer

792.6 K

Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.
- Free-energy change

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

- Standard free-energy change

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

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called Gibbs free energy (G). The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, ΔG = 0. If the process is spontaneous, ΔG < 0. If the process is not spontaneous as written but is spontaneous in the reverse direction, ΔG > 0. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free energy of formation (ΔG°_f), is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate ΔG^o for a reaction.

Contributors and Attributions

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2.E: Principles of Thermodynamics (Exercises)

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

Q3

Write detailed calculation down for each question involved in gambling,

a. How many “microstates” are there for the cards that come up from five random cards each from a separate deck?
b. What is the probability of getting 5 queens of hearts?
c. What is the probability of getting any specific hand of five cards?

Solution

Microstates are specific configurations in which each particle is distinguishable. The number of ways that they can be arranged to describe the macrostate is the weight of that macrostate and used in the definition of entropy.

a. The number of possible outcomes (microstates) of any repeated independent situation is equal to the number of possibilities in one iteration to the power of the repetitions. So in this case, the answer is 52 to the power of 5.
b. One of these 52^5 possibilities.
c. One of these 52^5 possibilities.

Q5

Is the above reaction spontaneous under 1 atm and room temperature? If so, what are the driving factors?

$$3\,\mathrm{NO\,(g)} \rightleftharpoons \mathrm{N_2O\,(g)} + \mathrm{NO_2\,(g)}$$

Solution

From a superficial overview of the reaction, we would conclude that the enthalpy change would be negative (i.e., $\Delta H < 0$) (why? more bonding in the products than the reactants). We would also expect a negative value of entropy ($\Delta n_{gas} < 0$. It is difficult to argue which would win from just looking at the reaction and we need to do a Hess's law like approach to solve numerically using the Gibbs energies of formation from Table T1:

$$\Delta^o G_{rxn} = \Delta^o G_f\{N_2O\} + \Delta G^o_f\{NO_2\} - 3\Delta G^o_f\{NO\}$$

Q9

For each of the following scenarios predict the system's entropy change whether it is $\Delta S < 0$, $\Delta S = 0$, or $\Delta S > 0$.

a. Increasing the amount of quarters being flipped from 2 to 4.
b. Moving a child from a 30 ft. × 30 ft. room to a 5 ft. × 5 ft. room to play in .
c. Increasing the temperature of a non-ideal polyatomic gas.

Solution

a. Increasing the amount of flipped quarters leads to ($\Delta S > 0$) because it increases the number of microstates available. For example: $2^2 = 4$ so 4 microstates possible with 2 quarters but $2^4 = 16$ so 16 microstates are available with four quarters. 16 > 4 so entropy would increase.
b. If you divided the room in 1 sq. ft cubes as the places where the child may stand/play, there are only 25 squares in which the child could stand so 25 microstates versus 900 squares/microstates in the other room. Therefore $\Delta S < 0$ because there are less microstates available.
c. Increasing the temperature of a non-ideal gas would lead to ($\Delta S > 0$) because the increased temperature would

"unfreeze" "frozen" modes in the gas, which would allow it more degrees of freedom and therefore microstates.

Q10

Determine whether the change in entropy for the processes listed down below are positive or negative:

a. condensing of iodine gas into a solid
b. diffusion of an ideal gas

Solution

a. Change in entropy is negative, as gaseous iodine turns solid, the decreased freedom of movement restricts the possible particle locations and hence there is a decrease in the number of microstates.
b. Change of entropy is positive. As diffusion occurs, there is increased freedom of movement and increase in the possible particle locations and an increase in the number of microstates.

Q11

Osmium melts at 3,027 °C and has an enthalpy change of fusion of 31.0 kJ/mol. Calculate the entropy of fusion of osmium.

Solution

Define the system at 1 mole of solid osmium at its melting point of 3027°C (3300 K). Imagine adding 31.0 kJ of heat infinitely slowly in such a way that the temperature remains constant, as the osmium melts. The heat is then equal to the q_{rev} for the melting. Substitute the value of heat supplied and T into the equation that defines the entropy of the change of the entropy of a system. Because the change occurs at a constant temperature, T may be outside the integral sign

$$\Delta S = \int \frac{dq_{rev}}{T} = \frac{1}{T}\int dq_{rev} = \frac{1}{T}q_{rev} = \frac{31.0 \times 10^3\ J\ mol^{-1}}{3300\ K} = 9.39\ J\ K^{-1}\ mol^{-1}$$

Tip. The temperature must be an absolute temperature (in Kelvins, for example).

Q13

Trouton's Rule is used to estimate the molar enthalpy of vaporization. What is iodine's enthalpy of vaporization if its normal boiling point is 184.4°C?

Solution

Trouton's Rule:

$$\Delta H_{vap} = \Delta S_{vap} T_b \tag{2.E.1506}$$

$$\Delta S_{vap} \approx 88 \frac{J}{Kmol} \tag{2.E.1507}$$

$$T_b = 184.4^o C = 457.55K \tag{2.E.1508}$$

$$\Delta H_{vap} = (88 \frac{J}{Kmol})(457.55K) = 40264.4 \frac{J}{mol} = 40.26 \frac{kJ}{mol} \tag{2.E.1509}$$

Enthalpy of vaporization of iodine is 40.26 kJ/mol

Q15

If 0.250 mol Argon is expanded reversibly and isothermally at 400 K in its compressible oven from an initial volume of 12.0 L to a final volume of 30.0 L, what will the ΔU, q, w, ΔH, and ΔS for the gas?

Solution

For an isothermal process, ΔU = 0, and consequently, ΔH = 0. However, for the work:

$$w = \int_{v_o}^{v_f} P\,dV$$

Where:

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

meaning that if we put P into terms of V using PV=nRT, then we can get the work, which comes out look like:

$$w = nRT \ln \frac{V_f}{V_o}$$

$$w = (0.250\ mol) \times (8.314\ \frac{\text{J}}{\text{Kmol}}) \times (400\ \text{K}) \times \ln \frac{30.0\ L}{12.0\ L} = 761.8\ \text{J}$$

$PV = nRT$ is the ideal gas law. it implies that the molecules or atoms of the gas are point masses, they have no volume and undergo only elastic collision.

Therefore, by the first law, the heat, q, must be be the negative of the work. Now, as for ΔS, we know:

$$\Delta S = \frac{-q}{T}$$

which implies that:

$$\Delta S = nR \ln \frac{V_f}{V_o}$$

$$\Delta S = (0.250\ \text{mol}) \times (8.314\ \frac{\text{J}}{\text{Kmol}}) \times \ln \frac{30.0\ \text{L}}{12.0\ \text{L}} = 1.90\ \frac{\text{J}}{\text{K}}$$

Q17

Consider this. Exactly 2 moles of ice undergoes three different processes.

I. heated reversibly at atmospheric pressure from temperature X to 0 °C, then
II. melted reversibly at 0 °C. Finally
II. it was heated reversibly at atmospheric pressure up to an unknown temperature Y.

Find temperature X & Y and identify ΔS_{surr}.

Given:

- ΔH_{fus} = 6007 J.mol^{-1}
- C_p (ice) = 38 J.K^{-1}.mol^{-1}
- C_p (water) = 75 J.K^{-1}.mol^{-1}
- ΔS_{I} = 12.034 J.K^{-1}
- ΔS_{III} = 136 J.K^{-1}

Solution

Since entropy changes are additive (thanks for them being state functions) and we have the entropy changes for Step I and Step III, all we need to do is calculate ΔS_{II}. However, we need to calculate temperatures first.

The equation below can be used to calculate ΔS_{sys} for a temperature change.

$$\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right) \tag{2.E.1510}$$

To solve for unknown temperature, the equation can be arranged in this way.

$$\exp(\frac{\Delta S}{nC_p}) = \frac{T_2}{T_1} \tag{2.E.1511}$$

Assuming the C_p stays constant throughout all the temperature change. Initial temperature X and final temperature Y can be found using the formula below.

$$T_x = T_2(\exp(\frac{\Delta S_{\mathrm{I}}}{nC_p}))^{-1} = (273.15K)(\exp(\frac{12.034J.K^{-1}}{(2.00mol)(38J.K^{-1}.mol^{-1})}))^{-1} = 233.15K \tag{2.E.1512}$$

$$T_y = T_1(\exp(\frac{\Delta S_{\mathrm{III}}}{nC_p})) = (273.15K)(\exp(\frac{136J.K^{-1}}{(2.00mol)(75J.K^{-1}.mol^{-1})})) = 298.15K \tag{2.E.1513}$$

ΔS_{II} must also be determined to obtain the $\Delta S_{\mathrm{system}}$.

Since the temperature remains constant in the second step, $\Delta S = q_{rev}$.

$$\Delta S_{\mathrm{II}} = 2\,mol \times \frac{6007\,J/mol}{273.15\,K} = 43.984\,J.K^{-1} \tag{2.E.1514}$$

Since the entire process is reversible,

$$\Delta \mathrm{S}_{\mathrm{surr}} + \Delta \mathrm{S}_{\mathrm{system}} = 0$$

so

$$\Delta \mathrm{S}_{\mathrm{surr}} = -\Delta \mathrm{S}_{\mathrm{system}}.$$

Now we add the three entropy changes:

$$-\Delta S_{\mathrm{system}} = -(\Delta S_{\mathrm{I}} + \Delta S_{\mathrm{II}} + \Delta S_{\mathrm{III}}) \tag{2.E.1515}$$

$$= -(12.034 + 54.98 + 136)J.K^{-1} \tag{2.E.1516}$$

$$= -80.15\,J.K^{-1} \tag{2.E.1517}$$

$$= \Delta S_{\mathrm{surr}} \tag{2.E.1518}$$

Q18

Suppose 2 moles of water at standard temperature (25°C) and pressure is spontaneously evaporated by allowing it to fall onto a nickel plate maintained at 125°C. Calculate ΔS for the water, ΔS for the nickel plate, and ΔS_{total} if $C_{p(\mathrm{H_2O})\,(\mathrm{l})}$= 75.4 J/(K.mol) and $C_{p(\mathrm{H_2O})\,(\mathrm{g})}$ = 36.0 J/(K.mol). Take ΔH_{vap} = 40.68 KJ/mol for water and its boiling point of 100°C.

Solution

$$q_1 = \Delta H = mc\Delta T = 2 \times 75.4\frac{J}{K.mol} \times (100 - 25) = 11310\ J \tag{2.E.1519}$$

$$q_2 = 40680\frac{J}{mol} \times 2 = 81.36 \times 10^3\ J \tag{2.E.1520}$$

$$q_3 = \Delta H = mc\Delta T = 2 \times 36\frac{J}{K.mol} \times (125 - 100) = 1800\ J \tag{2.E.1521}$$

$$q_{total} = 11310 + 81.36 \times 10^3 + 1800 = 94470\ J \tag{2.E.1522}$$

$$\Delta S_{\mathrm{H_2O}} = nC_{p(\mathrm{H_2O\,(l)})}) \ln\frac{T_2}{T_1} + nC_p(H_2O(g)) \ln\frac{T_2}{T_1} + n\frac{\Delta H}{T} \tag{2.E.1523}$$

$$= (2 \times 75.4 \times \ln \frac{373}{298}) + (2 \times 36 \times \ln \frac{398}{373}) + (2 \times \frac{40680}{373}) = 256.6 \frac{J}{K} \tag{2.E.1524}$$

$$\Delta S_{iron} = \frac{-94470 J}{398 K} = -237.4 \frac{J}{K} \tag{2.E.1525}$$

$$\Delta S_{tot} = \Delta S_{\mathrm{H_2O}} + \Delta S_{\mathrm{iron}} = 19.2 \frac{J}{K} \tag{2.E.1526}$$

Q19

A 181.49 g sample of lead at 97.0°C initially is added to a coffee cup calorimeter that contains 150.0 g water which is at 24.7°C. The equilibrium temperature is 29.4°C, assuming that there is no heat lost to the calorimeter or the environment. The molar heat capacity of lead (C_p(Pb)) is 26.4 J K^{-1} mol^{-1} and that of water (C_p(H_2O)) is 75.2 J K^{-1} mol^{-1}. What is ΔS for the lead sample, ΔS for the water sample, and ΔS_{total} for this process?

Solution

Since this progress is carried out at a constant pressure, and the temperature change for this progress doesn't include a phase transition, the relationship between the ΔS and the ΔT of a system can be described as:

$$\Delta S = nc_p ln \left(\frac{T_2}{T_1} \right) \tag{2.E.1527}$$

Convert the temperatures to Kelvin:

$$T_{equilibrium} = (29.4 + 273.15) K = 302.55\ K \tag{2.E.1528}$$

$$T_{initial,\ Pb} = (97.0 + 273.15) K = 370.15\ K \tag{2.E.1529}$$

$$T_{initial,\ H_2O} = (24.7 + 273.15) K = 297.85\ K \tag{2.E.1530}$$

Calculate the amount of moles of the substance present:

$$n_{Pb} = 181.49\ g\ Pb \times \frac{1\ mol\ Pb}{207.2\ g\ Pb} = 0.8759\ mol\ Pb \tag{2.E.1531}$$

$$n_{H_2O} = 150.0\ g\ H_2O \times \frac{1\ mol\ H_2O}{18.02\ g\ H_2O} = 8.324\ mol\ H_2O \tag{2.E.1532}$$

The given molar heat capacities:

$$C_{p,\ Pb} = 26.4 \frac{J}{K \cdot mol} \tag{2.E.1533}$$

$$C_{p,\ H_2O} = 75.2 \frac{J}{K \cdot mol} \tag{2.E.1534}$$

Substitute the known variables into the equation: $\Delta S = nc_p ln \left(\frac{T_2}{T_1} \right)$

$$\Delta S_{Pb} = nc_{p,Pb} ln \left(\frac{T_{equilibrium}}{T_{inital,\ Pb}} \right) \tag{2.E.1535}$$

$$\Delta S_{Pb} = 0.8759\ mol\ Pb \times 26.4 \frac{J}{K \cdot mol} \times ln \left(\frac{302.55\ K}{370.15\ K} \right) = -4.66\ \frac{J}{K} \tag{2.E.1536}$$

$$\Delta S_{H_2O} = nc_{p,H_2O} ln \left(\frac{T_{equilibrium}}{T_{inital,\ H_2O}} \right) \tag{2.E.1537}$$

$$\Delta S_{H_2O} = 8.324\ mol\ H_2O \times 75.2 \frac{J}{K \cdot mol} \times ln \left(\frac{302.55\ K}{297.85\ K} \right) = 9.80\ \frac{J}{K} \tag{2.E.1538}$$

$$\Delta S_{total} = \Delta S_{Pb} + \Delta S_{H_2O} = (-4.66 + 9.80)\ \frac{J}{K} = 5.14\ \frac{J}{K} \tag{2.E.1539}$$

Q20

Copper has a heat capacity of 38.5 J K^{-1} mol^{-1}, approximately independent of temperature between 0°C to 100°C. Calculate the enthalpy and entropy change of 5.00 moles of copper as it is cooled at atmospheric pressure from 100°C to 0°C.

Solution

$$\Delta H = q = nC_p\Delta T \tag{2.E.1540}$$

$$= (5.00\ mol)(38.5\ \frac{J}{K.mol})(273\ K–373\ K)$$

$$\Delta H = -19250\ J$$

$$\Delta S = nC_p ln(\frac{T_2}{T_1}) \tag{2.E.1541}$$

$$= (38.5\frac{J}{K.mol})\ln(\frac{273\ K}{373\ K})(5.00\ mol)$$

$$= -60.1\frac{J}{K}$$

Q23

The alkaline earth metals react with oxygen to give the following compounds:

$$2\,\mathrm{Be\,(g)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{BeO\,(s)}$$

$$2\,\mathrm{Mg\,(g)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{MgO\,(s)}$$

$$2\,\mathrm{Ca\,(g)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{CaO\,(s)}$$

Compute ΔS for each reaction, and identify a periodic trend about the entropy.

Solution

All the values you need to solve this problem are in the back of the Oxtoby textbook, so just find the numbers needed and use the formula:

$$\sum S^o_{products} - \sum S^o_{reactants} = \Delta S^o_{rxn}$$

$$2Be_{(g)} + O_{2(g)} \rightarrow 2BeO_{(s)}$$

$$2(14.14) - (2(136.16) + 205.03) = -449.07\frac{\mathrm{J}}{\mathrm{K.mol}}$$

$$2Mg_{(g)} + O_{2(g)} \rightarrow 2MgO_{(s)}$$

$$2(26.92) - (2(148.54) + 205.03) = -448.27\frac{\mathrm{J}}{\mathrm{K.mol}}$$

$$2Ca_{(g)} + O_{2(g)} \rightarrow 2CaO_{(s)}$$

$$2(39.75) - (2(154.77) + 205.03) = -435.07\frac{\mathrm{J}}{\mathrm{K.mol}}$$

The entropy of the reaction decreases as you go up the periodic table.

Q27

Is the entropy change in the reaction positive, negative or zero and why?

$$\mathrm{CH_4\,(g) + 2\,O_2\,(g) \longrightarrow CO_2\,(g) + 2\,H_2O\,(l)}$$

Hint: You don't need to actually calculate the change in entropy to determine whether the change in entropy is positive or negative. Think about it conceptually.

Solution

The answer is negative because the number of gas molecules decreases. Gas molecules have more entropy than liquid molecules since they have more energy in the form of degrees of freedom of motion (translational, rotational, and vibrational). Therefore, fewer gas molecules mean less entropy.

Q33

At $25.0°\mathrm{C}$ the reaction below is not spontaneous.

$$\mathrm{2\,H_2O\,(g) \longrightarrow 2\,H_2\,(g) + O_2\,(g)}$$

with ΔG = $+228.59\ \frac{kJ}{mol}$

If the above reaction were coupled with the following nonspontaneous reaction, could it be made to proceed? Why or Why not?

$$\mathrm{3\,H_2\,(g) + N_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$$

with ΔG = $-16.48\ \frac{kJ}{mol}$

Solution

Coupling the nonspontaneous reaction

$$\mathrm{2\,H_2O_{(g)} \rightleftharpoons 2\,H_{2\,(g)} + O_{2\,(g)}}$$

with $\Delta G = +228.59\ \frac{kJ}{mol}$

for a spontaneous reaction (ΔG) is negative.

$$\mathrm{3\,H_{2(g)} + N_{2(g)} \rightleftharpoons 2\,NH_{3(g)}}$$

with $\Delta G = -16.48\ \frac{kJ}{mol}$

yields

$$\mathrm{2\,H_2O_{(g)} + \cancel{3}\,H_{2(g)} + N_{2(g)} \rightleftharpoons \cancel{2H_{2\,(g)}} + O_{2\,(g)} + 2\,NH_{3(g)}}$$

with ΔG = $+212.11\ \frac{kJ}{mol}$

Since ΔG is positive, we know the reaction is still not spontaneous after being coupled with a spontaneous reaction

Q35A

A reaction at constant temperature and pressure is spontaneous if $\Delta G < 0$ and nonspontaneous if $\Delta G > 0$. Over what range of temperatures is each of the following processes spontaneous? Assume that all gases are at a pressure of 1 atm. (Hint: Use Tables T1 to calculate ΔH and ΔS (assumed independent of temperature and equal to $\Delta H°$ and $\Delta S°$, respectively, and then use the definition of ΔG).

a. Photosynthesis, a reaction of how plants produce food for themselves and animals, and convert carbon dioxide into water:

$$6\,CO_2\,(g) + 6\,H_2O\,(l) + \text{light} \longrightarrow C_6H_{12}O_6\,(s) + 6\,O_2\,(g)$$

b. The combustion reaction of propane, found in gas grills and some fireplaces:

$$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$$

c. Methane burning in O_2 gas.

$$CH_4\,(g) + 2\,O_2\,(g) \longrightarrow CO_2\,(g) + 2\,H_2O\,(l)$$

Solution

a. First calculate ΔH° and $\Delta S^\circ$of the reaction $6\,CO_2\,(g) + 6\,H_2O\,(l) + \text{light} \longrightarrow C_6H_{12}O_6\,(s) + 6\,O_2\,(g)$ from the data in Tables T1.

$$\Delta H^\circ = -1273.3 + (6 \times 0) - (6 \times -393.5) - (6 \times -285.8) = 2802.5\ \frac{kJ}{mol}$$

$$\Delta S^\circ = 212.1 + (6 \times 205.2) - (6 \times 213.8) - (6 \times 70) = -259.5\ \frac{J}{mol.K}$$

Since the problem asks for the temperature range in which the reaction is spontaneous. The changeover from spontaneity to non-spontaneity occurs at $\Delta G^\circ = 0$. To find the temperature the makes $\Delta G^\circ = 0$, the relationship of $\Delta G^\circ = \Delta H^\circ - T\ \Delta S^\circ$ will be used. Remember to convert ΔS° to $kJ\ mol^{-1}$ (or ΔH° to $J\ mol^{-1}$) so that the units cancel out properly.

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{2802.5\ \frac{kJ}{mol}}{0.2595\ \frac{kJ}{mol.K}} = 10799.6\ K$$

Because ΔH° and ΔS° are both positive, the reaction is spontaneous at temperatures above 10799.6 K.

Reviewer Note: The solution is incorrect here. Because $\Delta H^\circ > 0$ and $\Delta S^\circ < 0$, the reaction is never spontaneous.

b. Perform similar calculations for the reaction $C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$

$$\Delta H^\circ = (3 \times -393.5) + (4 \times -285.83) + 103.8 - (5 \times 0) = -2220.02\ \frac{kJ}{mol}$$

$$\Delta S^\circ = (3 \times 28) + (4 \times 70) - 270.3 - (5 \times 205.2) = -374.9\ \frac{J}{mol.K}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{2220.02\ \frac{kJ}{mol}}{0.3749\ \frac{kJ}{mol.K}} = 5922\ K$$

Since ΔH° and ΔS° are both negative, the reaction is spontaneous below 5922 K.

c. The reaction $CH_4\,(g) + 2\,O_2\,(g) \longrightarrow CO_2\,(g) + 2\,H_2O\,(l)$

$$\Delta H^\circ = (-393.5) + (2 \times -285.8) + 74.6 - (2 \times 0) = -890.5\ \frac{kJ}{mol}$$

$$\Delta S^\circ = (28) + (2 \times 70) - 186.3 - (2 \times 205.2) = -242.9\ \frac{J}{mol.K}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-890.5\ \frac{kJ}{mol}}{-0.2429\ \frac{kJ}{mol.K}} = 3666\ K$$

Since ΔH° and ΔS° are both negative, the reaction is spontaneous below 3666 K.

Q35B

Over what temperatures are these reactions spontaneous (under constant pressure and temperature)? You may need to use Table 1.

a. $\mathrm{S\,(s, rhombic) + Zn\,(s) \rightarrow ZnS\,(s, sphalerite)}$
b. $\mathrm{2\,Cu\,(s) + Cl_2 \rightarrow 2\,CuCl\,(s)}$
c. $\mathrm{4\,Al\,(s) + 3\,O_2\,(g) \rightarrow 2\,Al_2O_3\,(s)}$

Answer

By calculating ΔH_{rxn} and ΔS_{rxn} un der standard conditions and at 25°C, we can calculate the range of temperature in which ΔG is positive and therefore spontaneous. To calculate ΔH_{rxn} and ΔS_{rxn}, we use Hess's Law , in which:

$$\Delta H_{rxn} = \sum nH_{products} - \sum nH_{reactants}$$

$$\Delta S_{rxn} = \sum nS_{products} - \sum nS_{reactants}$$

a)

$$\mathrm{\Delta H_{rxn} = -206.0 – (0 + 0) = -206.0 \frac{kJ}{mol}}$$

$$\mathrm{\Delta S_{rxn} = 57.7 – (41.6 + 32.1) = -16 \frac{J}{K.mol}}$$

$$\mathrm{\Delta G_{rxn} = -206.0 - T(-0.016)}$$

From here, we can set T = 0 because we know that ΔG must be < 0 to be a spontaneous reaction.

T<12875K

b)

$$\mathrm{\Delta H_{rxn} = (2 \times -137.2) – (0 + 0) = -274.4 \frac{kJ}{mol}}$$

$$\mathrm{\Delta S_{rxn} = (2 \times 86.2) – ((2 \times 33.2) + 223.1) = -117.1 \frac{J}{K.mol}}$$

$$\mathrm{\Delta G_{rxn} = -274.4 - T(-0.1171)}$$

T < 2343.3K

c)

$$\mathrm{\Delta H_{rxn} = (2(-1675.7)) - (0 + 0) = -3351.4 \frac{kJ}{mol}}$$

$$\mathrm{\Delta S_{rxn} = (2(50.92) – (4(28.3) + (3(205.2)) = -626.96 \frac{J}{K.mol}}$$

$$\mathrm{\Delta G_{rxn} = -3351.4 - T(-0.62696)}$$

T < 5345.5K

Q37

Determine if the following reaction is spontaneous at 25°C by evaluating $\Delta H°_{rxn}$, $\Delta S°_{rxn}$ and $\Delta G°_{rxn}$.

$$\mathrm{N_2H_4\,(l) + O_2\,(g) \longrightarrow N_2\,(g) + 2\,H_2O\,(l)}$$

Solution

- $\Delta \mathrm{H}^{\circ}_{\mathrm{rxn}} = 0 + (2 \times -285.8) – 0 – 50.6 = 622.2 \frac{\mathrm{kJ}}{\mathrm{mol}}$
- $\Delta \mathrm{S}^{\circ}_{\mathrm{rxn}} = (2 \times 70.0) + 191.6 – 205.2 – 121.2 = 5.2 \frac{\mathrm{J}}{\mathrm{mol.K}}$
- $\Delta \mathrm{G}^{\circ}_{\mathrm{rxn}} = -622.2 – (25 + 273.15)(0.0052) = -623.8 \frac{\mathrm{kJ}}{\mathrm{mol}}$

=> Spontaneous ($\Delta G^{\circ}_{rxn} < 0$)

Q39

A thermodynamic engine operates cyclically and reversibly between two temperatures reservoirs, absorbing heat from the high-temperature bath at 600 K and discarding heat to low-temperature bath at 300 K.

a. What is the thermodynamic efficiency of the engine?
b. How much heat is absorbed from the high-temperature bath if -1800 J of heat is discarded to the low-temperature bath during each cycle?
c. How much work does the engine perform in one cycle of operation?

Solution

(a)

$$\text{Thermodynamic efficiency} = \frac{(\mathrm{T}_1 – \mathrm{T}_2)}{\mathrm{T}_1}$$

$$\frac{(600\ \mathrm{K} – 300\ \mathrm{K})}{(600\ \mathrm{K})} \times 100\% = 50\%$$

(b)

$$\frac{1800\ \mathrm{J}}{50\%} = 3600\ \mathrm{J}$$

(c)

$$-3600\ \mathrm{J} \times 50\% = -1800\ \mathrm{J}$$

Q41

Acetone ($\mathrm{C_3H_6O}$) is an volatile liquid with a normal boiling point of 56°C and a molar enthalpy of vaporization of 29.1 kJ $\mathrm{mol^{-1}}$. What is the molar entropy of vaporization of acetone under 1 atm of pressure?

Solution

First we need the write the equation relating entropy and enthalpy:

$$\Delta G_{vap} = \Delta H_{vap} – T \Delta S_{vap}$$

As a result of the process of normal boiling being at quilibrium $\Delta G = 0$ so all that needs to be done is T in Kelvin and ΔH_{vap} needs to be plugged in and then we solve for ΔS_{vap}:

$$0 = 29.1\ \frac{\mathrm{kJ}}{\mathrm{mol}} – (329\ \mathrm{K})(\Delta \mathrm{S_{vap}})$$

$$\Delta \mathrm{S_{vap}} = 88.45 \frac{\mathrm{J}}{\mathrm{K.mol}}$$

Q53

Under standard conditions and 25°C, you have this reversible process

$$\mathrm{Sn\,(s, white)} \longrightarrow \mathrm{Sn\,(s, gray)}$$

a. Is the change in entropy (ΔS) for this reaction positive or negative? Calculate the change in entropy using Table T1.
b. Calculate (ΔS) for the reaction if ΔH for this reaction is -2.1 kJ/mol.

Solution

For part a), we use the formula

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

Plugging in the values from Table T1 gives us

$$\Delta S = 44.1 - 55.2 = -7.1 \frac{J}{mol \cdot K}$$

For part b), we use the formula for a reversible process

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

$$\Delta S = \frac{-2100\ J/mol}{298.15\ K}$$

$$\Delta S = -7.04 \frac{J}{mol \cdot K}$$

Q59

Compute the ΔG_f° for the following reaction the reaction. The ΔG_f° of H_2SO_3 (aq) is -537.81 kJ mol^{-1}, the ΔG_f° of SO_2 (g) is -300.19 kJ mol^{-1}, and the ΔG_f° of H_2O (g) is -120.42 kJ mol^{-1}.

$$\mathrm{H_2SO_3\,(aq) \longrightarrow H_2O\,(g) + SO_2\,(g)}$$

Solution

ΔG° for the reaction is equal to the sum of the G_f° for the products minus the sum of the G_f° for the reactants.

$$\Delta G^{\circ} = \left(-300.19 \frac{kJ}{mol} + -120.42 \frac{kJ}{mol}\right) - \left(-537.81 \frac{kJ}{mol}\right)$$

$$\Delta G^{\circ} = 117.2 \frac{kJ}{mol}$$

Q61

Professor Nesral wants to create some water through the combustion of hydrogen. This reaction is depicted as follows:

$$\mathrm{2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(g)}$$

Is this reaction spontaneous? Prove it by calculating ΔG° at 298.15K. Suppose that Nesral asks his friend in El Azizia, Libya, where the temperature is around $57^{\circ}C$ (330K), to perform the same reaction. Calculate the Gibbs energy for this value and compare it to ΔG°.

Relevant Information:

Entropy Values (S°; $\frac{J}{mol\,K}$)

- Hydrogen: 130.6
- Water: 188.7
- Oxygen: 205.6

Enthalpy Values(H°; $\frac{kJ}{mol}$)

- ΔH_f° Water: -241.826

Solution

From intuition, the equation shows that 3 moles of gas, 2 moles of $\mathrm{H_2}$ and 1 mole of $\mathrm{O_2}$, are reacting to form 2 moles of $\mathrm{H_2O}$ gas. This is a decrease in entropy, which may hint at the reaction being non spontaneous. ΔG° should still be calculated to make sure.

The information provided is the entropic values of the product and reactants, and the enthalpy of water. If the ΔS° is calculated, then the ΔG° can also be found using the following equation:

$$\Delta G = \Delta H^\circ_{rxn} – T\Delta S^\circ_{rxn}.$$

Where ΔH°_{rxn} is the Heat and ΔS°_{rxn} is the entropy of the reaction under standard conditions (constant pressure), and T is temperature. Knowing that ΔS°_{rxn} is a state variable, it can be calculated as the difference between the sum of the entropy values of the products and reactants multiplied by their coefficients (This is known as Hess's Law). In other words,

$$\Delta S^\circ = \sum n_{products} \times S^\circ_{f_{products}} - \sum n_{reactants} \times S^\circ_{f_{reactants}}$$

From this, ΔS°_{rxn} can be calculated as such:

$$\Delta S^\circ = \left(2 \times 188.7 \frac{J}{molK}\right) - \left(\left[2 \times 130.6 \frac{J}{molK}\right] + \left[205.6 \frac{J}{molK}\right]\right)$$

$$= -89.4 \frac{J}{mol.K}$$

Since both H_2 and O_2 are in their natural states, the H_f° associated with them equals to zero. Since enthalpy (ΔH°_{rxn}) is also a state variable, it can be calculated with Hess's Law as well.

$$\Delta H^\circ = \left(2 \times -241.826 \frac{kJ}{mol}\right) - \left(\left[0 \frac{kJ}{mol}\right] + \left[0 \frac{kJ}{mol}\right]\right)$$

$$\Delta H^\circ = -483.652 \frac{kJ}{mol}$$

Plugging in these values, as well as the temperature, $298.15K$, will yield ΔG°.

$$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} – T\Delta S^\circ_{rxn}.$$

$$\Delta G^\circ_{rxn} = -483.652 \frac{kJ}{mol} – 298.15K \left(-0.0894 \frac{kJ}{mol.K}\right).$$

$$\Delta G^\circ_{rxn} = -456.99739 \frac{kJ}{mol}$$

The ΔG_{rxn} is therefore $-456.99739 \frac{kJ}{mol}$. This very negative value means that the reaction is DEFINITELY spontaneous. It also makes sense on a conceptual level because combustion reaction like these release a lot of heat, which means that the process if enthalpically driven! Calculating the ΔG_{rxn} at a different temperature, as mentioned in the problem, has the same method:

$$\Delta G_{rxn} = \Delta H^\circ_{rxn} – T\Delta S^\circ_{rxn}.$$

$$\Delta G_{rxn} = -483.652 \frac{kJ}{mol} – 330K \left(-0.0894 \frac{kJ}{mol.K}\right).$$

$$\Delta G_{rxn} = -454.15 \frac{kJ}{mol}$$

In both situations the ΔG_{rxn} is very negative, but in the hotter climate it is slightly less so. What this shows is that, at a higher temperatures the entropic factors contribute more to the gibbs energy than at standard conditions. This

showcases the temperature dependence of entropy. In another reaction that released less energy, this difference may have made the reaction non-spontaneous!

Abstract : Hess's Law to find ΔG_{rxn}.

Q63A

The concentration of sodium in the plasma is approximately 0.14 M. While in the fluid outside of the plasma, sodium concentration is about 0.5 M.

a. In what direction will the sodium ions spontaneously move past the cell wall?
b. The spontaneous process of movement in part a is called "passive transport". Movement in the opposite direction is called "active transport" and requires work to happen. Calculate the amount of free energy required to move 5 moles of Na^+ by active transport (non-spontaneous direction) at 273 K.

Solution

a) The Na^+ ions will spontaneously flow into the plasma because it flows from high to low concentration.

b) $\Delta \mathrm{G} = \mathrm{nRT} \ln \frac{\mathrm{c_2}}{\mathrm{c_1}}$ where c_2 is the destination of Na^+ after active transport occurs while c_1 is the original concentration of the Na^+ ions.

$$\Delta \mathrm{G} = (5 \text{ mole})(8.3145 \tfrac{\mathrm{J}}{\mathrm{K.mol}})(273 \text{ K}) \ln \tfrac{0.5}{0.14}$$

$$\Delta \mathrm{G} = 14447.26 \text{ J}$$

Q63B

For a hypothetical nerve cell, the sodium ion concentration is 0.015 M outside the cell and 0.00045 M inside the cell. Active transport involves using proteins and chemical energy stored in ATP to move the ions in a thermodynamically unfavorable direction. Assuming that conditions in the cell allow the hydrolysis of a single ATP molecule to give 2.05×10^{-18} J of usable enegy. How many molecules of ATP would be needed to move 0.005 moles of sodium ions using active transport at standard conditions? You can assume that the sodium ion concentrations remain constant.

Solution

To answer this question, the change of free energy is needed which means the following equation is needed

$$\Delta G = -RTlnQ$$

$$R = 8.314 \ \frac{J}{mol.K} \qquad T = 298K \qquad Q = \frac{[Na^+]_{in}}{[Na^+]_{out}}$$

$$\Delta G = -8.314 \ \frac{J}{mol.K} \times 298K \times ln(\frac{0.00045 \ M}{0.015 \ M})$$

$$\Delta G = -2424 \ \frac{J}{mol} \times ln(0.03) = 8688 \ \frac{J}{mol}$$

Now that we have the the free energy, we can determine the number of ATP molecules needed

$$8688 \ \frac{J}{mol} \times 0.005 \ mol = 43.4 \ J$$

$$\frac{43.4 \ J}{2.05 \times 10^{-18} \ J \ molecule^{-1}} = 2.119 \times 10^{19} \ \text{ ATP molecules}$$

Answer: 2.119×10^{19} ATP molecules

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UNIT II: PHYSICAL EQUILIBRIA

Macroscopic quantities of matter can exist in only one of three states: Gas, Liquid or Solid. The following are not states of matter: electricity, gels, powders, plasmas, supercritical fluids or your mother's apple pie. Only *two* aspects determine the state of matter for a specific system/chemical: 1) The (intermolecular) forces within the sample and 2) the conditions outside the sample (e.g. temperature, pressure etc).

III: Solids, Liquids, and Phase Transitions

3.1: Bulk Properties of Gases, Liquids, and Solids - Molecular Interpretation
3.2: Intermolecular Forces - Origins in Molecular Structure
3.3: Intermolecular Forces in Liquids
3.4: Phase Equilibrium
3.5: Phase Transitions
3.6: Phase Diagrams
3.7: Clausius-Clapeyron Equation
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3.E: Solids, Liquids, and Phase Transitions (Exercises)

IV: Solutions

4.0: Types of Solutions - Some Terminology
4.1: Composition of Solutions
4.2: Nature of Dissolved Species
4.3: Phase Equilibrium in Solutions - Nonvolatile Solutes
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4.5: Separating Volatile Solutions - Distillation
4.6: Colloidal Suspensions
4.E: Solutions (Exercises)

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III: SOLIDS, LIQUIDS, AND PHASE TRANSITIONS

3.1: Bulk Properties of Gases, Liquids, and Solids - Molecular Interpretation

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3.9: Bonding in Metals

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

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3.1: Bulk Properties of Gases, Liquids, and Solids - Molecular Interpretation

Learning Objectives

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

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

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

Surface Tension

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

Figure $3.1.1$ presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads. A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.

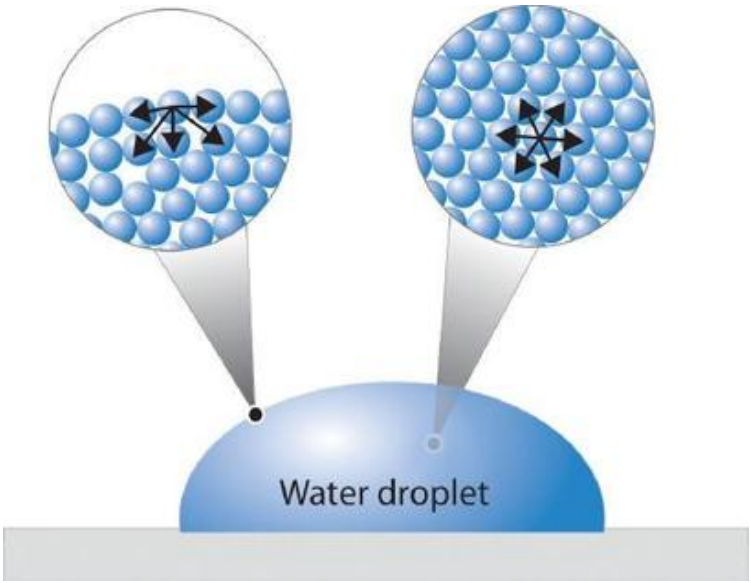


Figure 3.1.1: A Representation of Surface Tension in a Liquid. Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces. (CC BY-SA-NC; anonymous)

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it "floats," even though steel is much denser than water. Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking. This is better demonstrated in the zero-gravity conditions of space (Figure 3.1.2).

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

https://www.youtube.com/embed/o8TssbmY-GM?vq=hd1080

Figure 3.1.2: The Effects of the High Surface Tension of Liquid Water. The Full video can be found at https://youtu.be/o8TssbmY-GM.

Such phenomena are manifestations of surface tension, which is defined as the energy required to increase the surface area of a liquid by a specific amount. Surface tension is therefore measured as energy per unit area, such as joules per square meter (J/m^2). The values of the surface tension of some representative liquids are listed in Table 3.1.2. Note the correlation between the surface tension of a liquid and the strength of the intermolecular forces: the stronger the intermolecular forces, the higher the surface tension. For example, water, with its strong intermolecular hydrogen bonding, has one of the highest surface tension values of any liquid, whereas low-boiling-point organic molecules, which have relatively weak intermolecular forces, have much lower surface tensions. Mercury is an apparent anomaly, but its very high surface tension is due to the presence of strong metallic bonding.

Table 3.1.2: Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids

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

Substance	Surface Tension (× 10^{-3} J/m^2)	Viscosity (mPa•s)	Vapor Pressure (mmHg)	Normal Boiling Point (°C)
20°C	72.8	1.00	17.5	—
60°C	66.2	0.47	149	—
100°C	58.9	0.28	760	—

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

Surface Energies and Surface Tension

Any material - solid, liquid or (non-ideal) gas - wants to bond to itself. This is why condensed phase materials "sticks" together in the first place. However, a surface disrupts this bonding, and so incurs an energy penalty. This is why liquids in zero gravity ball up into spherical drops (Figure 3.1.2) - the sphere is the shape with the lowest surface area for a fixed volume. We can describe this *surface energy* with dimensions of energy per unit area, which is the amount of extra energy needed to create new surface or extend a surface (e.g., cracking a solid or parting a liquid). Hence, surface tension is typically given in J/m^2 units (Table 3.1.2).

Capillary Action

Intermolecular forces also cause a phenomenon called capillary action, which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure 3.1.3. When a glass capillary is put into a dish of water, water is drawn up into the tube. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises. The height of the water does *not* depend on the angle at which the capillary is tilted.

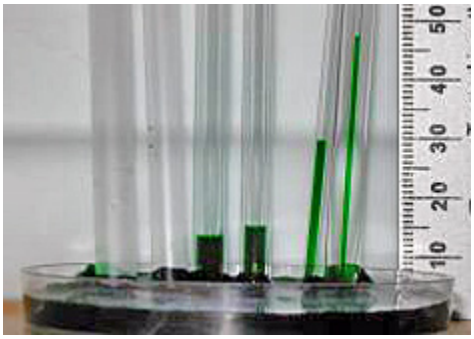


Figure 3.1.3: The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters. (Dr. Clay Robinson, PhD, West Texas A&M University)

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

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

Water has both strong adhesion to glass, which contains polar SiOH groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while

adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (part (a) in Figure 3.1.4). The upper surface of a liquid in a tube is called the meniscus, and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex (Figure 3.1.4*b*).

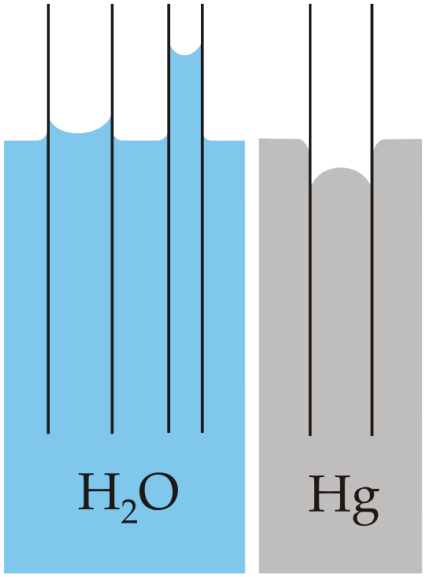


Figure 3.1.4: The Phenomenon of Capillary Action. Capillary action of water compared to mercury, in each case with respect to a polar surface such as glass. (a) This drawing illustrates the shape of the meniscus and the relative height of a mercury column when a glass capillary is put into liquid mercury. The meniscus is convex and the surface of the liquid inside the tube is *lower* than the level of the liquid outside the tube. (b) Because water adheres strongly to the polar surface of glass, it has a concave meniscus, whereas mercury, which does not adhere to the glass, has a convex meniscus. (CC BY-SA 3.0; MesserWoland via Wikipedia)

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

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

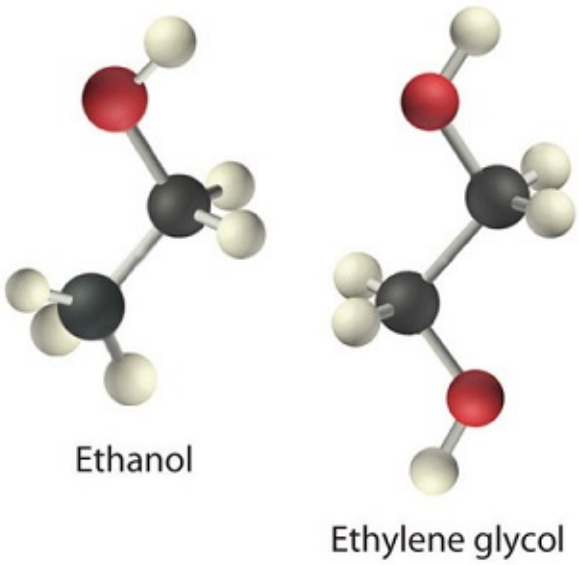
Viscosity

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

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

The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa•s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table 3.1.1 and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($HOCH_2CH_2OH$), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can

form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.



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

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

Viscosity increases as intermolecular interactions or molecular size increases.

Application: Motor Oils

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine must effectively lubricate under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an engine in the heat of the Mojave Desert in August. Viscosity decreases rapidly with increasing temperatures because the kinetic energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing (Table 3.1.3). As a result, an oil that is thin enough to be a good lubricant in a cold engine will become too "thin" (have too low a viscosity) to be effective at high temperatures.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

https://www.youtube.com/embed/V5a4kP-5Jiw?vq=hd1080

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

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

Table 3.1.3: Dynamic Viscosity (N s/m^2)

SAE	Temperature (^oC)			
	0	20	50	100
10	0.31	0.079	0.020	0.005
20	0.72	0.170	0.033	0.007
30	1.53	0.310	0.061	0.010
40	2.61	0.430	0.072	0.012
50	3.82	0.630	0.097	0.015

Example 3.1.1

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

Given: substance and composition of the glass surface

Asked for: behavior of oil and the shape of meniscus

Strategy:

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

Solution:

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

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

Exercise 3.1.1

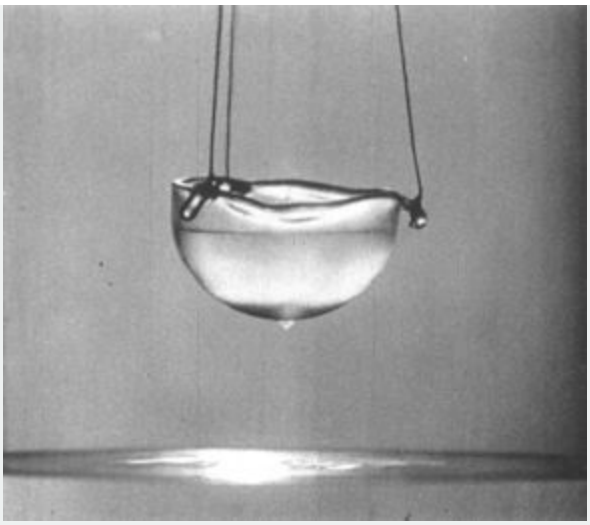
Predict what will happen when a glass capillary is put into a beaker of ethylene glycol. Will the ethylene glycol be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)?

Answer

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

Oddity of Science: Superfluid Helium-4

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



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

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

Boiling Points

The **vapor pressure** of a liquid is defined as the pressure exerted by a vapor in equilibrium with its condensed phases (solid or liquid) at a given temperature in a closed system (discussed in more detail in next Sections of Chapter). As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point of the liquid. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure $3.1.8$ are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm.

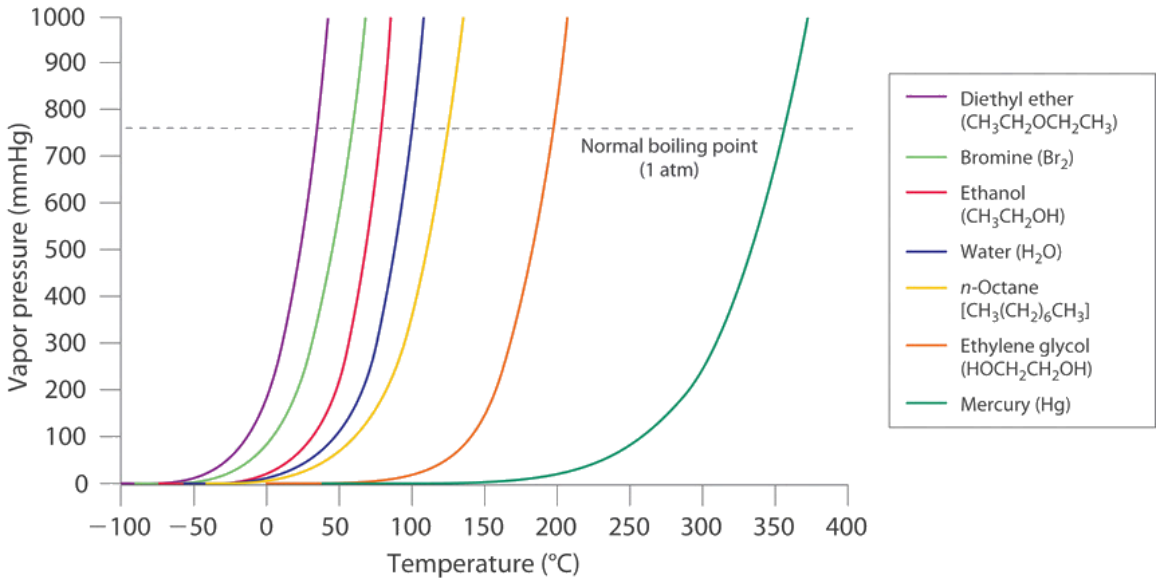


Figure 3.1.8: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC; anonymous)

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

Table 3.1.4: The Boiling Points of Water at Various Locations on Earth

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

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 mmHg, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 mmHg in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C, respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table 3.1.4 lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a “three-minute egg” may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

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

Example 3.1.2: Boiling Mercury

Use Figure 3.1.8 to estimate the following.

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

YouTube Video

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View this YouTube Video online
https://www.youtube.com/embed/0PIZUjhzrKw?vq=hd1080

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

Given: data in Figure 3.1.8, pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure 3.1.8 and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.
B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

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

Exercise 3.1.2: Boiling Ethylene Glycol

Ethylene glycol is an organic compound primarily used as a raw material in the manufacture of polyester fibers and fabric industry, and polyethylene terephthalate resins (PET) used in bottling. Use the data in Figure 3.1.8 to estimate the following.

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

Answer a

200°C

Answer b

450 mmHg

Summary

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

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

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3.2: Intermolecular Forces - Origins in Molecular Structure

Learning Objectives

- To describe the intermolecular forces in liquids.

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

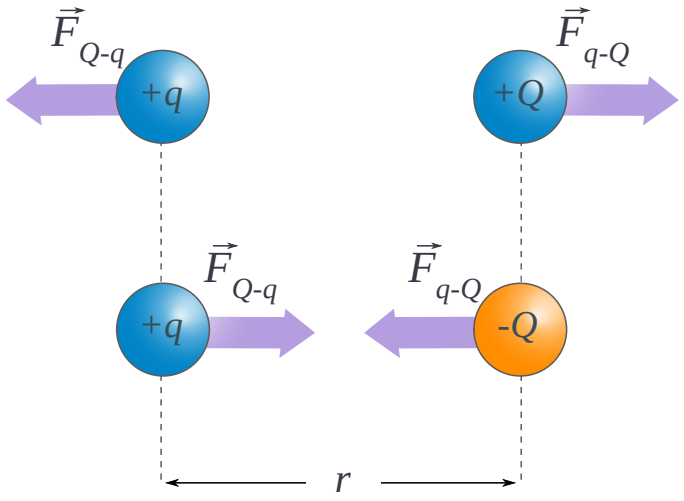
> The properties of liquids are intermediate between those of gases and solids but are more similar to solids.

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

Coulombic Interactions

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

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



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

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

[redacted]

In this mathematical representation of Coulomb's observations,

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

From Equation 3.2.1066, the electrostatic force between two charges is *inversely* proportional to the *square* of the distance separating the two atoms.

Ion–Ion Interactions

The interactions between ions (ion - ion interactions or charge-charge interactions) are the easiest to understand since such interactions are just a simple application of Coulombic forces (Equation 3.2.1066). This specific interaction operates over relatively long distances in the gas phase and is responsible for the attraction of opposite charge ions and the repulsion of like charged ions.

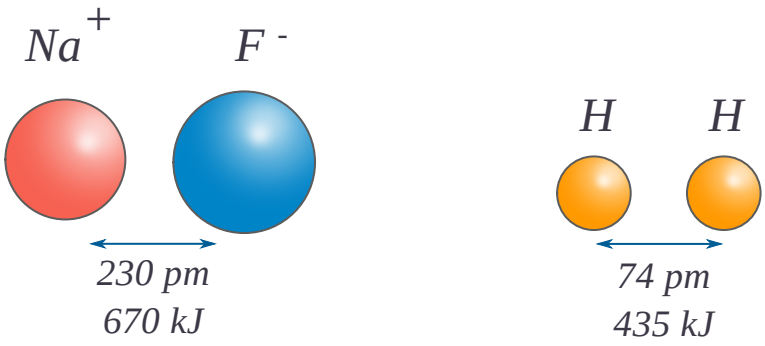


Figure 3.2.1: Ion-Ion attraction in NaF (left) exceeds the covalent bond energy of $\mathrm{H_2}$ (right). (CC BY-NC; Ümit Kaya)

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

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

[redacted]

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

Figure 3.2.2: Ion - Ion Interactions in the Gas Phase. (Gary L. Bertrand).

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

Equation 3.2.1067 is an example of an *inverse square law*; the force falls off as the square of the distance. A similar law governs the manner in which the illumination falls off as you move away from a point light source; recall this the next time you walk away from a street light at night, and you will have some feeling for what an inverse square law means.

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

[redacted]

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

[redacted]

Example 3.2.1

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

Solution

The interactions involved in forming NaCl dimers is the ion-ion forces with a potential energy given by Equation 3.2.1069. However, this is the energy of interaction for one pair of Na^+ and Cl^- ion and needs to be scaled by a mole. So the energy released will be

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

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

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

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

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

Ion-Dipole Interactions

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

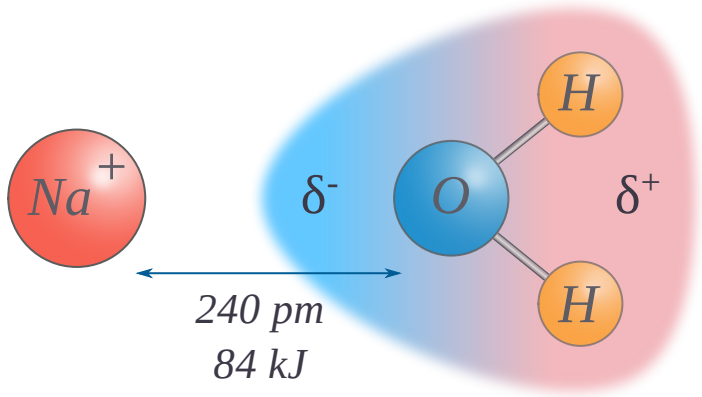


Figure 3.2.3: Ion - Dipole Interaction. (CC BY-NC; Ümit Kaya)

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

Since there is now both attractive and repulsive interactions and they both get weaker as the ion and dipole distance increases while also approaching each other in strength, the net ion-dipole is an inverse square relationship as shown in Equation 3.2.1070.

[redacted]

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

[redacted]

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

Ion-Ion vs. Ion-Dipole potentials

There are several differences between ion-ion potential (Equation 3.2.1069) and the ion-dipole potential (Equation 3.2.1070) interactions.

- First, the potential of ion/dipole interactions are negative and net interaction will always be attractive, since the attraction of the opposite dipole to the ion will make it closer than the dipole with the like charge. By using the absolute value of the charge of the ion, and placing a negative sign in front of the equation, this results in a lowering of the potential energy (μ is positive).
- Second, the potential drops off quicker in Equation 3.2.1070, where it is an inverse square relationship to the radius ($1/r^2$), while a simple charge-charge interaction (Equation 3.2.1069) has a linear inverse relationship ($1/r$). This means the ion-dipole are a shorter range interaction and diminish more rapidly the father the polar molecule is from the ion.
- Third, note that the units of the two equations are the same, as μ has the units of charge X distance. However, the distance in μ is the distance between the dipoles of the polar molecule, while the distance denoted by the "r" is the distance between the ion and the dipole.

It needs to be understood that the molecules in a solution are rotating and vibrating and actual systems are quite complicated (Figure 3.2.4). What is important to realize is that these interactions are Coulombic in nature and how the mathematical equations describe this in terms of the magnitude of the charges and their distances from each other. In this course we will not be calculating dipole moments or the magnitudes of them, but understanding how to read the equations, and developing qualitative understandings that allow us to predict trends.

Figure 3.2.4: Ion-Dipole Interactions in the gas phase. (Gary L. Bertrand).

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in part (a) in Figure 3.2.1.

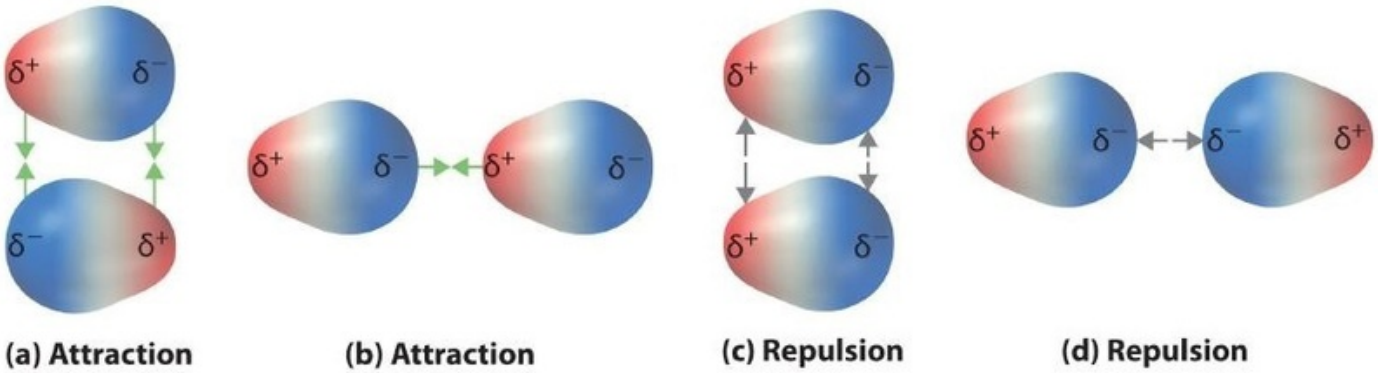


Figure 3.2.5: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure 3.2.1*c*). Hence dipole–dipole interactions, such as those in Figure 3.2.5*b*, are *attractive intermolecular interactions*, whereas those in Figure 3.2.5*d* are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 3.2.2. On average, however, the attractive interactions dominate.

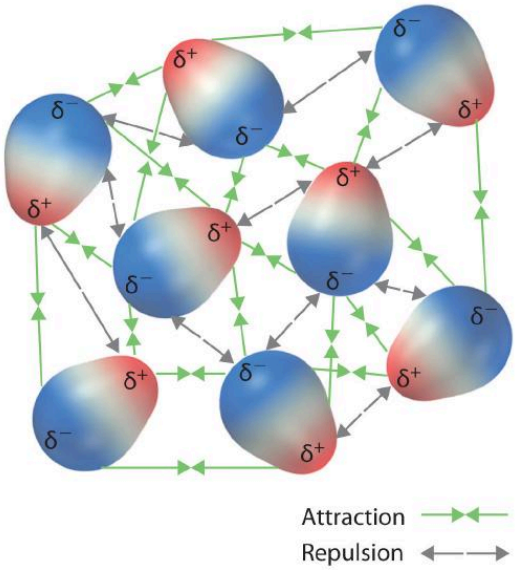


Figure 3.2.6: Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

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

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

[redacted]

Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a

series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 3.2.1. Using what we learned about predicting relative bond polarities from the electronegativities of the bonded atoms, we can make educated guesses about the relative boiling points of similar molecules.

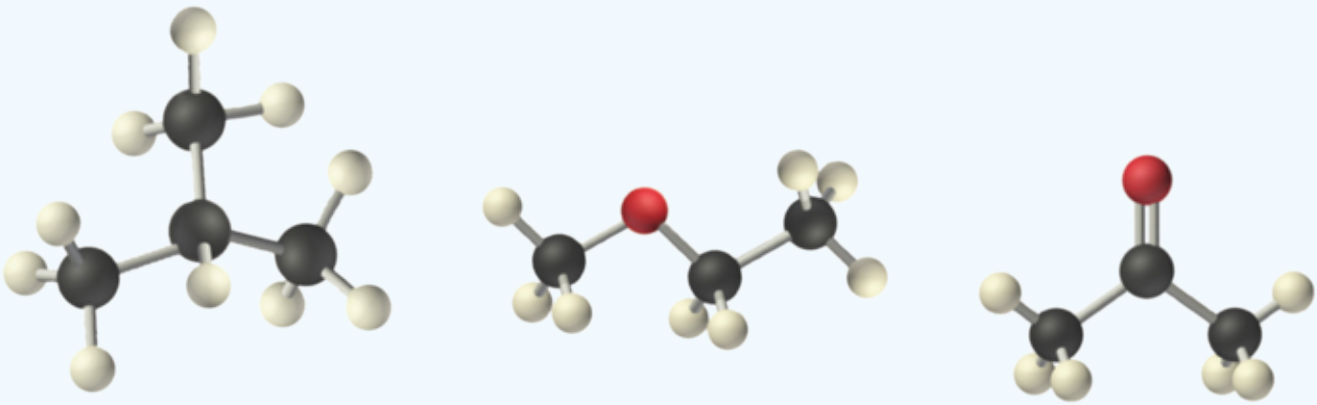
Table 3.2.1: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

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

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

Example 3.2.2

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



2-Methylpropane Ethyl methyl ether Acetone

Given: compounds

Asked for: order of increasing boiling points

Strategy:

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

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds. The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment

and a very low boiling point. Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point. Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point. Thus we predict the following order of boiling points: 2-methylpropane < ethyl methyl ether < acetone. This result is in good agreement with the actual data: 2-methylpropane, boiling point = –11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

Exercise 3.2.1

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

Answer

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

London Dispersion Forces

Thus far we have considered only interactions between polar molecules, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 3.2.2).

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

Table 3.2.2: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

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

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 3.2.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to

show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.

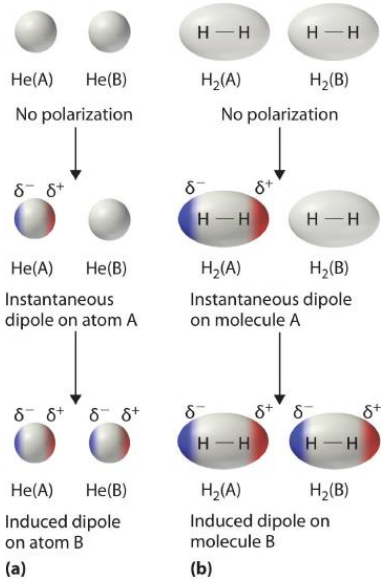


Figure 3.2.3: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure 3.2.3, tends to become more pronounced as atomic and molecular masses increase (Table 3.2.2). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1s electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

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

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 3.2.4). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 3.2.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

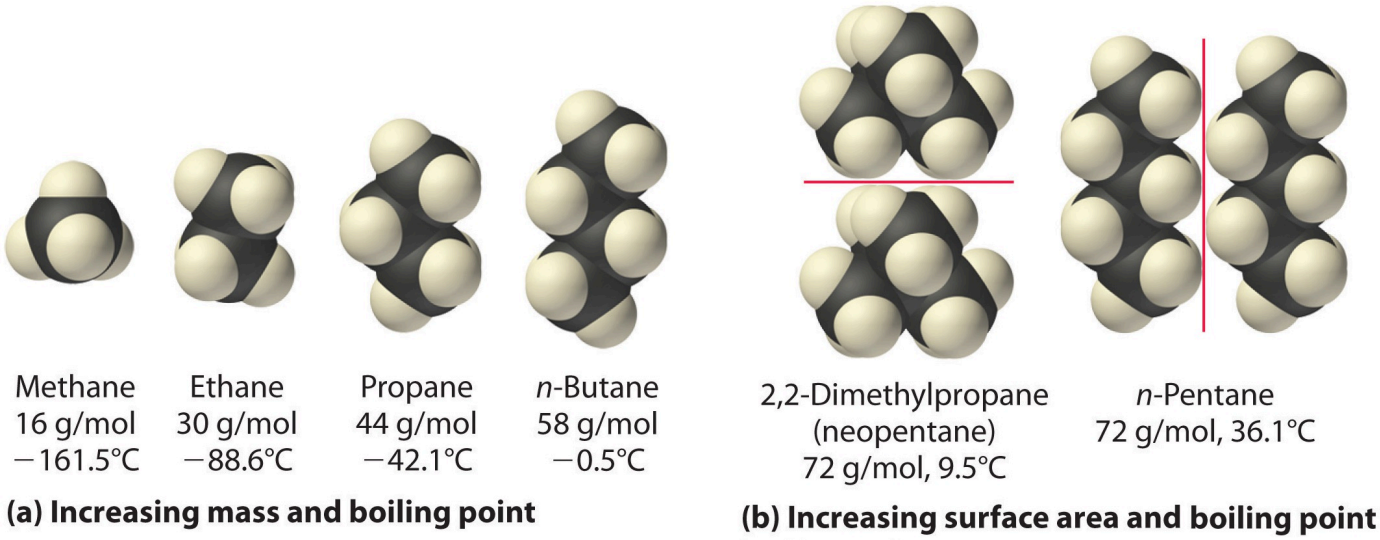


Figure 3.2.4: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

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

Example 3.2.2

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

Given: compounds

Asked for: order of increasing boiling points

Strategy:

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

Solution:

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

Exercise 3.2.2

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

Answer

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

Summary

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

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3.3: Intermolecular Forces in Liquids

Learning Objectives

- To describe the intermolecular forces in liquids.

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 3.3.1. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of –130°C for water! Imagine the implications for life on Earth if water boiled at –130°C rather than 100°C.

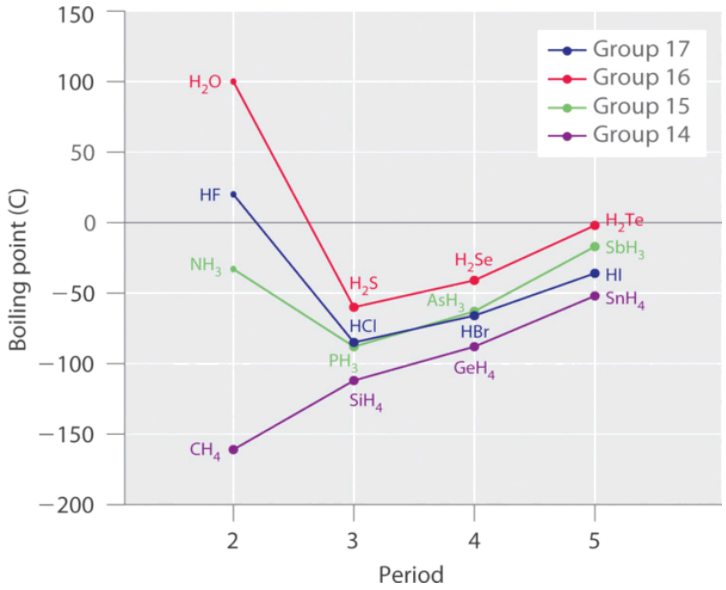


Figure 3.3.1: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure 3.3.2 . A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they

connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O · · · H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

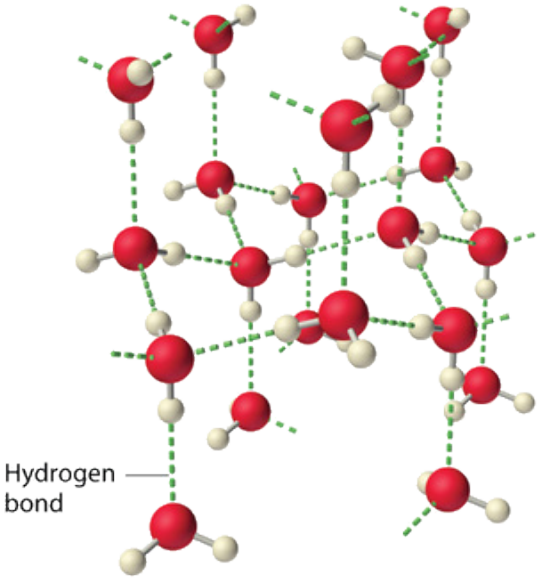


Figure 3.3.2: The Hydrogen-Bonded Structure of Ice

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

It takes two to tango...

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

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

Example 3.3.1

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

Given: compounds

Asked for: formation of hydrogen bonds and structure

Strategy:

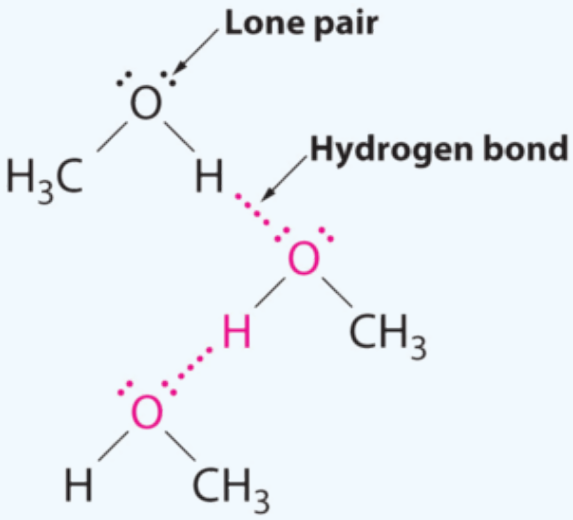
A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

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

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



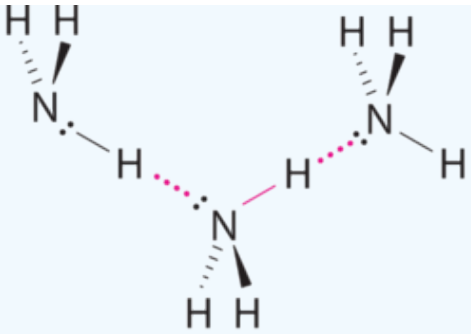
Hydrogen bonding in methanol

Exercise 3.3.1

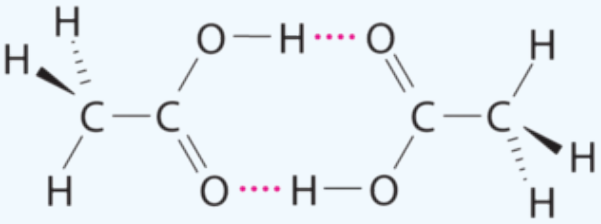
Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia

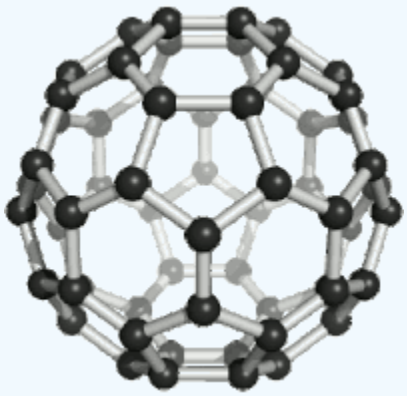


Hydrogen bonding in acetic acid

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

Example 3.3.2

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



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

Given: compounds

Asked for: order of increasing boiling points

Strategy:

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

Solution:

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion

forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses:

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

Exercise 3.3.2

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

Answer

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

Special Properties of Water

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

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

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

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

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



Figure 3.3.3: Young boy with father ice fish. The fish do not freeze below the ice surface of the lake due to the unique properties of water. (Public Domain; U.S. Fish and Wildlife Service).

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

Summary

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

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3.4: Phase Equilibrium

Learning Objectives

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

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

Evaporation and Condensation

Because the molecules of a liquid are in constant motion, we can plot the fraction of molecules with a given kinetic energy (*KE*) against their kinetic energy to obtain the kinetic energy distribution of the molecules in the liquid (Figure $3.4.1$), just as we did for a gas. As for gases, increasing the temperature increases both the average kinetic energy of the particles in a liquid and the range of kinetic energy of the individual molecules. If we assume that a minimum amount of energy (E_0) is needed to overcome the intermolecular attractive forces that hold a liquid together, then some fraction of molecules in the liquid always has a kinetic energy greater than E_0. The fraction of molecules with a kinetic energy greater than this minimum value increases with increasing temperature. Any molecule with a kinetic energy greater than E_0 has enough energy to overcome the forces holding it in the liquid and escape into the vapor phase. Before it can do so, however, a molecule must also be at the surface of the liquid, where it is physically possible for it to leave the liquid surface; that is, only molecules at the surface can undergo evaporation (or vaporization), where molecules gain sufficient energy to enter a gaseous state above a liquid's surface, thereby creating a vapor pressure.

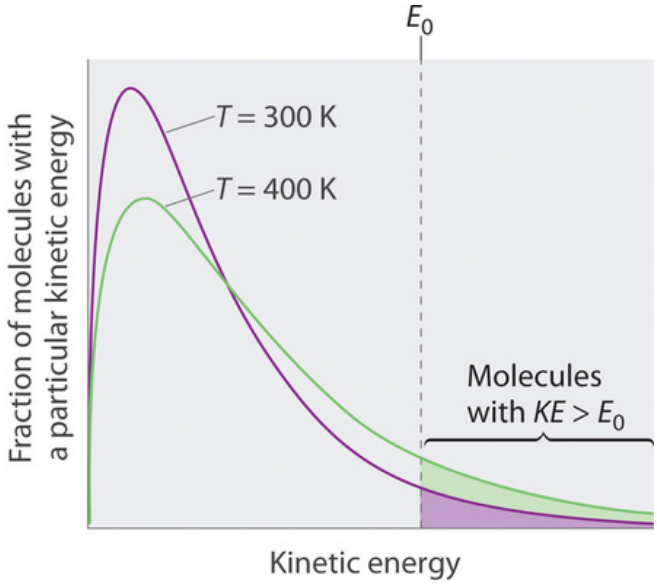


Figure 3.4.1: The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures. Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature. (CC BY-SA-NC; Anonymous by request)

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

To understand the causes of vapor pressure, consider the apparatus shown in Figure 3.4.2. When a liquid is introduced into an evacuated chamber (part (a) in Figure 3.4.2), the initial pressure above the liquid is approximately zero because there are as yet no molecules in the vapor phase. Some molecules at the surface, however, will have sufficient kinetic energy to escape from the liquid and form a vapor, thus increasing the pressure inside the container. As long as the temperature of the liquid is held constant, the fraction of molecules with $KE > E_0$ will not change, and the rate at which molecules escape from the liquid into the vapor phase will depend only on the surface area of the liquid phase.

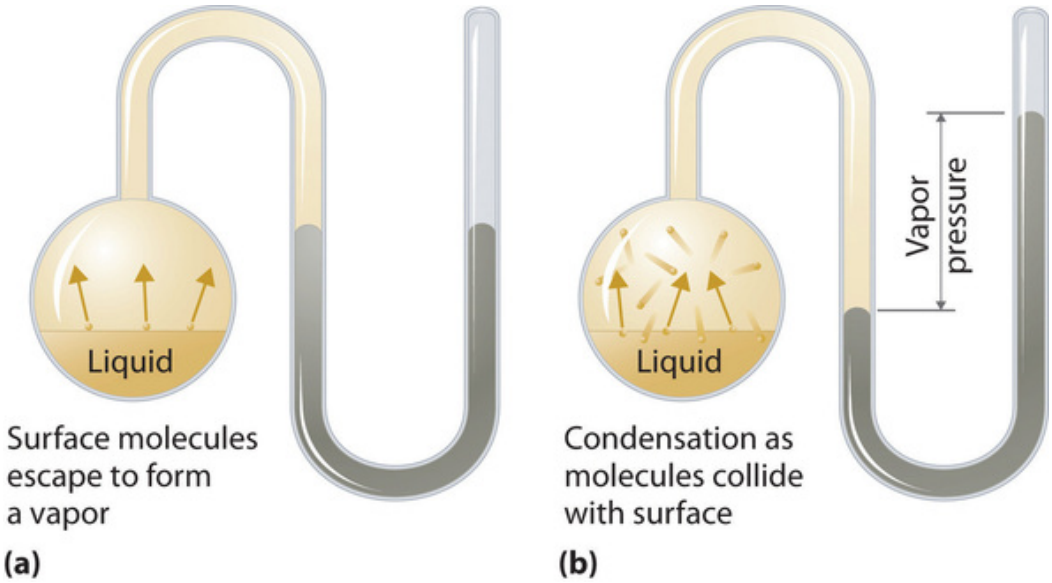


Figure 3.4.2: Vapor Pressure. (a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant. (CC BY-SA-NC; Anonymous by request)

As soon as some vapor has formed, a fraction of the molecules in the vapor phase will collide with the surface of the liquid and reenter the liquid phase in a process known as condensation (part (b) in Figure 3.4.2). As the number of molecules in the

vapor phase increases, the number of collisions between vapor-phase molecules and the surface will also increase. Eventually, a *steady state* will be reached in which exactly as many molecules per unit time leave the surface of the liquid (vaporize) as collide with it (condense). At this point, the pressure over the liquid stops increasing and remains constant at a particular value that is characteristic of the liquid at a given temperature. The rates of evaporation and condensation over time for a system such as this are shown graphically in Figure 3.4.3.

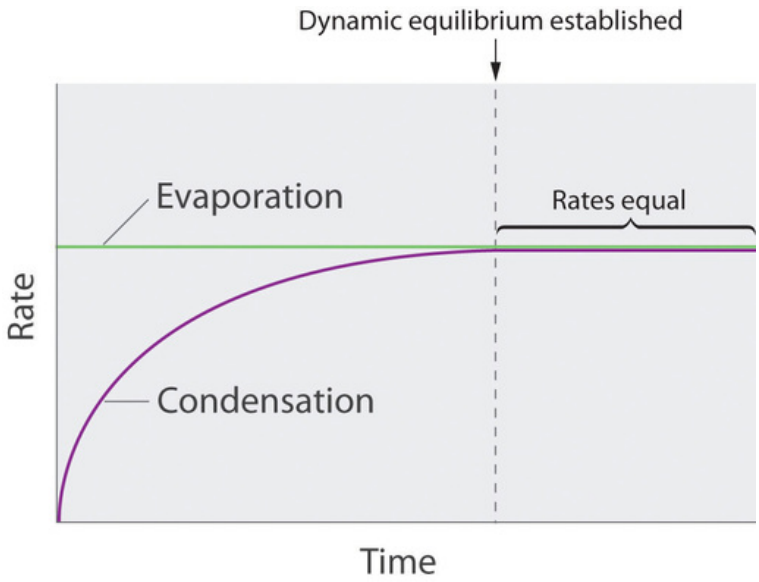


Figure 3.4.3: The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber. The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation. (CC BY-SA-NC; Anonymous by request)

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

Equilibrium Vapor Pressure

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

If a liquid is in an *open* container, however, most of the molecules that escape into the vapor phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and an equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it has “disappeared.” The speed with which this occurs depends on the vapor pressure of the liquid and the temperature. Volatile liquids have relatively high vapor pressures and tend to evaporate readily; nonvolatile liquids have low vapor pressures and evaporate more slowly. Although the dividing line between volatile and nonvolatile liquids is not clear-cut, as a general guideline, we can say that substances with vapor pressures greater than that of water (Figure 3.4.4) are relatively volatile, whereas those with vapor pressures less than that of water are relatively nonvolatile. Thus diethyl ether (ethyl ether), acetone, and gasoline are volatile, but mercury, ethylene glycol, and motor oil are nonvolatile.

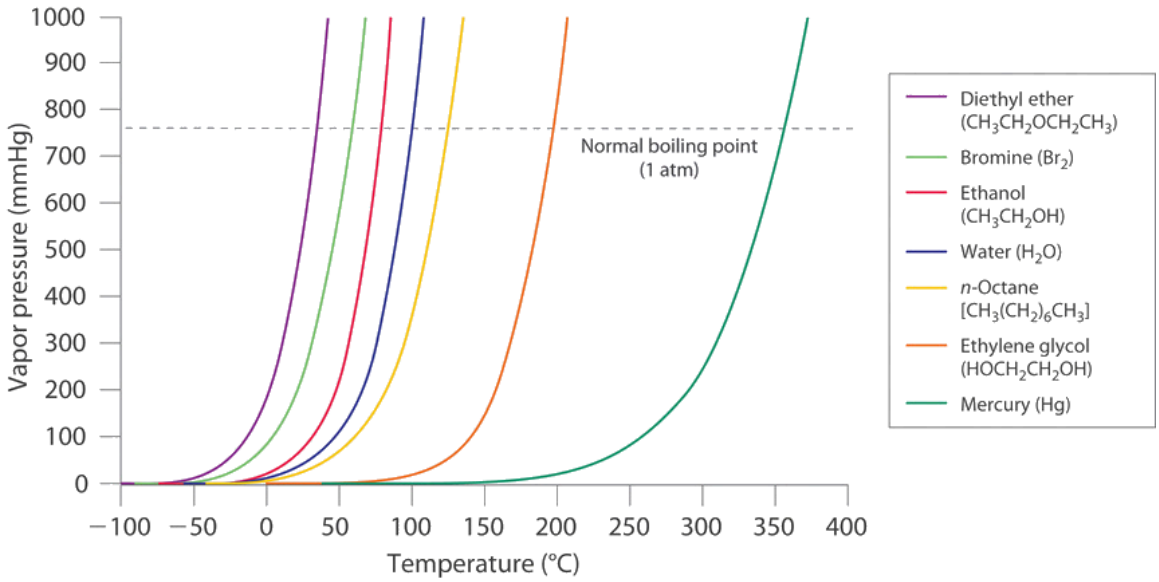


Figure 3.4.4: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC; Anonymous by request)

The equilibrium vapor pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point. It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapor pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure 3.4.4. Molecules that can hydrogen bond, such as ethylene glycol, have a much lower equilibrium vapor pressure than those that cannot, such as octane. The nonlinear increase in vapor pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. The temperature dependence is so strong because the vapor pressure depends on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid, and this fraction increases exponentially with temperature. As a result, sealed containers of volatile liquids are potential bombs if subjected to large increases in temperature. The gas tanks on automobiles are vented, for example, so that a car won't explode when parked in the sun. Similarly, the small cans (1–5 gallons) used to transport gasoline are required by law to have a pop-off pressure release.

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

YouTube Video

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View this YouTube Video online
https://www.youtube.com/embed/4QtcdpfRO1M?vq=hd1080

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

The exponential rise in vapor pressure with increasing temperature in Figure $3.4.4$ allows us to use natural logarithms to express the nonlinear relationship as a linear one.

[redacted]

where

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

Plotting $\ln P$ versus the inverse of the absolute temperature $(1/T)$ is a straight line with a slope of $-\Delta H_{vap}/R$. Equation $1.1.1$, called the Clausius–Clapeyron Equation, can be used to calculate the ΔH_{vap} of a liquid from its measured vapor pressure at two or more temperatures. The simplest way to determine ΔH_{vap} is to measure the vapor pressure of a liquid at **two** temperatures and insert the values of P and T for these points into Equation $1.1.2$, which is derived from the Clausius–Clapeyron equation:

[redacted]

Conversely, if we know ΔH_{vap} and the vapor pressure P_1 at any temperature T_1, we can use Equation $1.1.2$ to calculate the vapor pressure P_2 at any other temperature T_2, as shown in Example $3.4.1$.

YouTube Video

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

Example 3.4.1: Vapor Pressure of Mercury

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

experimentally measured vapor pressures of liquid Hg at four temperatures

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

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

Given: vapor pressures at four temperatures

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

Strategy:

A. Use Equation 1.1.2 to obtain ΔH_{vap} directly from two pairs of values in the table, making sure to convert all values to the appropriate units.
B. Substitute the calculated value of ΔH_{vap} into Equation 1.1.2 to obtain the unknown pressure (P_2).

Solution:

A The table gives the measured vapor pressures of liquid Hg for four temperatures. Although one way to proceed would be to plot the data using Equation 1.1.1 and find the value of ΔH_{vap} from the slope of the line, an alternative approach is to use Equation 1.1.2 to obtain ΔH_{vap} directly from two pairs of values listed in the table, assuming no errors in our measurement. We therefore select two sets of values from the table and convert the temperatures from degrees Celsius to kelvin because the equation requires absolute temperatures. Substituting the values measured at 80.0°C (T_1) and 120.0°C (T_2) into Equation 1.1.2 gives

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

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

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

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

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

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

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

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

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

$$P_2 = 4.21 Torr$$

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

Exercise 3.4.1: Vapor Pressure of Nickel

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

Answer

1896°C

Boiling Points

As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point of the liquid. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure 3.4.4 are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm. Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils

below 100°C.

Table 3.4.1: The Boiling Points of Water at Various Locations on Earth

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

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 mmHg, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 mmHg in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C, respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table 3.4.1 lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a "three-minute egg" may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

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

Example 3.4.2: Boiling Mercury

Use Figure 3.4.4 to estimate the following.

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



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

Given: Data in Figure 3.4.4, pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure 3.4.4 and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.
B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

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

Exercise 3.4.2: Boiling Ethlyene Glycol

Ethylene glycol is an organic compound primarily used as a raw material in the manufacture of polyester fibers and fabric industry, and polyethylene terephthalate resins (PET) used in bottling. Use the data in Figure 3.4.4 to estimate the following.

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

Answer a

200°C

Answer b

450 mmHg

Summary

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

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

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3.5: Phase Transitions

Learning Objectives

- To calculate the energy changes that accompany phase changes.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These changes of state are often called phase changes. The six most common phase changes are shown in Figure 3.5.1.

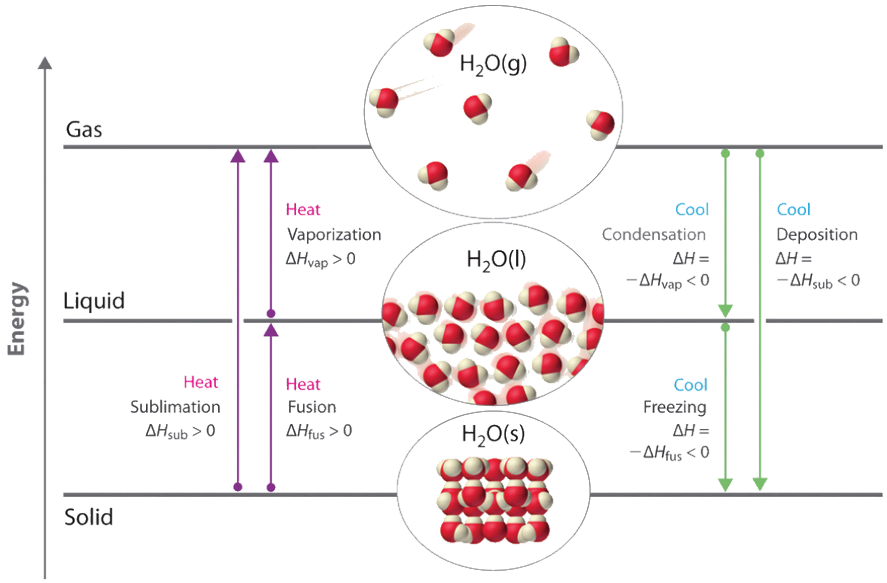


Figure 3.5.1: Enthalpy changes that accompany phase transitions are indicated by purple and green arrows. Purple arrows indicate heating from solid to gas, solid to liquid, and liquid to gas. Green arrows indicate cooling from gas to solid, gas to liquid, and liquid to solid. (CC BY-SA-NC; anoymous)

Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the energy of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very disordered, have the weakest. Thus any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; it is **endothermic**. Conversely, any transition from a less ordered to a more ordered state (liquid to solid, gas to liquid, or gas to solid) releases energy; it is **exothermic**. The energy change associated with each common phase change is shown in Figure 3.5.1.

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

Previously, we defined the enthalpy changes associated with various chemical and physical processes. The melting points and molar **enthalpies of fusion** (ΔH_{fus}), the energy required to convert from a solid to a liquid, a process known as fusion (or melting), as well as the normal boiling points and enthalpies of vaporization (ΔH_{vap}) of selected compounds are listed in Table 3.5.1.

Table 3.5.1: Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances. Values given under 1 atm. of external pressure.

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

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

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



Figure 3.5.2: The Sublimation of solid iodine. When solid iodine is heated at ordinary atmospheric pressure, it sublimes. When the I_2 vapor comes in contact with a cold surface, it deposits I_2 crystals. Figure used with permission from Wikipedia.

The direct conversion of a solid to a gas, without an intervening liquid phase, is called sublimation. The amount of energy required to sublime 1 mol of a pure solid is the enthalpy of sublimation (ΔH_{sub}). Common substances that sublime at standard temperature and pressure (STP; 0°C, 1 atm) include CO_2 (dry ice); iodine (Figure 3.5.2); naphthalene, a substance used to protect woolen clothing against moths; and 1,4-dichlorobenzene. As shown in Figure 3.5.1, the enthalpy of sublimation of a substance is the sum of its enthalpies of fusion and vaporization provided all values are at the same *T*; this is an application of Hess's law.

Fusion, vaporization, and sublimation are endothermic processes; they occur only with the absorption of heat. Anyone who has

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

Temperature Curves

The processes on the right side of Figure 3.5.1—freezing, condensation, and deposition, which are the reverse of fusion, sublimation, and vaporization—are exothermic. Thus heat pumps that use refrigerants are essentially air-conditioners running in reverse. Heat from the environment is used to vaporize the refrigerant, which is then condensed to a liquid in coils within a house to provide heat. The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

Heating Curves

Figure 3.5.3 shows a heating curve, a plot of temperature versus heating time, for a 75 g sample of water. The sample is initially ice at 1 atm and –23°C; as heat is added, the temperature of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s) of ice, which is the number of joules required to raise the temperature of 1 g of ice by 1°C. As the temperature of the ice increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of water is *greater* than that of ice. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

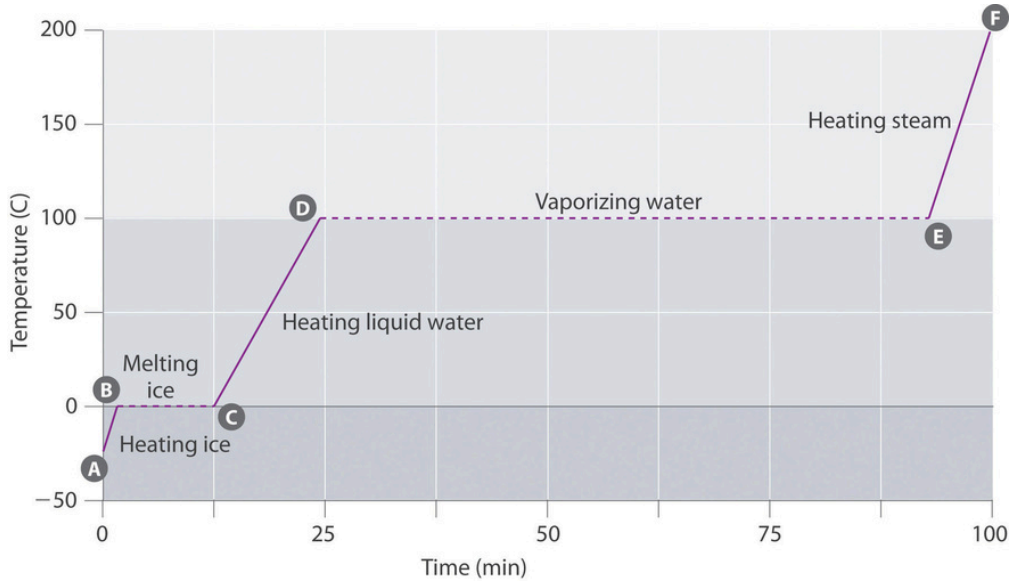


Figure 3.5.3: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and –23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

Thus *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively

to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

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

If heat is added at a constant rate, as in Figure 3.5.3, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure 3.5.3, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

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

Cooling Curves

The cooling curve, a plot of temperature versus cooling time, in Figure 3.5.4 plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled. Although we might expect the cooling curve to be the mirror image of the heating curve in Figure 3.5.3, the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquid. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystal), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

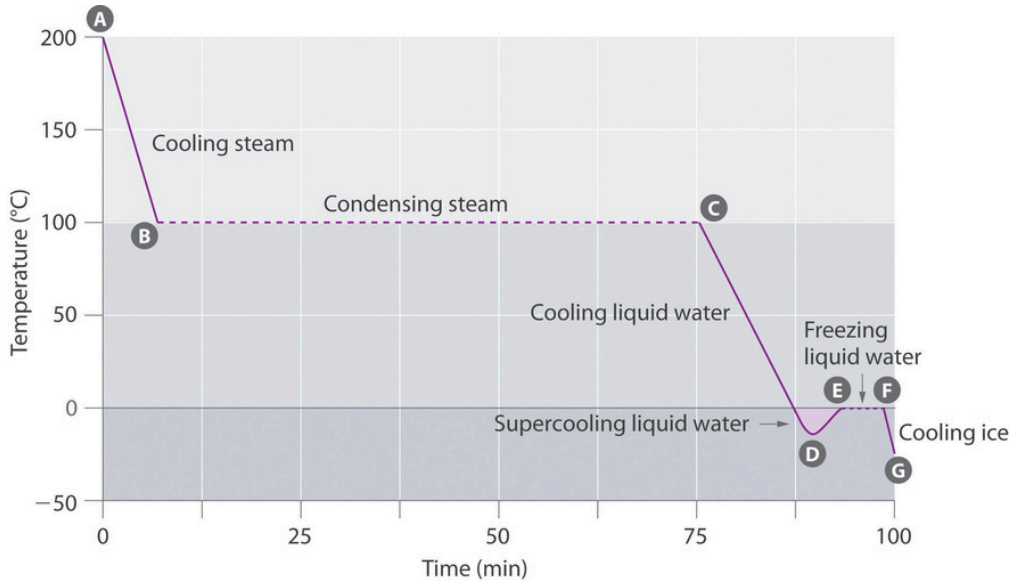


Figure 3.5.4: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth’s climate. For example, supercooling of water droplets in clouds can prevent

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

YouTube Video

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

Example 3.5.1: Cooling Tea

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

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

Asked for: final temperature

Strategy

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

Solution

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

$$q = mC_s\Delta T$$

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

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

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

For our 50.0 g ice cube:

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

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

$$\begin{aligned} q_{tea} &= -16,700J = 500mL \cdot \frac{1.00\,g}{1\,mL} \cdot 4.184J/(g\,\bullet°C)\Delta T \\ \Delta T &= -7.98°C = T_f - T_i \\ &= 12.02°C \end{aligned}$$

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

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

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

$$209.2J/°C \cdot T_f = -2092J/°C \cdot T_f + 25,150J$$

$$2301.2J/°C \cdot T_f = 25,150J$$

$$T_f = 10.9°C$$

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

Exercise 3.5.1: Death by Freezing

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at −5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you cannot remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at −5.0°C to your body's internal temperature of 37°C. Use the data in Example 3.5.1

Answer

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

Summary

Fusion, vaporization, and sublimation are endothermic processes, whereas freezing, condensation, and deposition are exothermic processes. Changes of state are examples of **phase changes**, or *phase transitions*. All phase changes are accompanied by changes in the energy of a system. Changes from a more-ordered state to a less-ordered state (such as a liquid to a gas) are *endothermic*. Changes from a less-ordered state to a more-ordered state (such as a liquid to a solid) are always *exothermic*. The conversion of a solid to a liquid is called **fusion (or melting)**. The energy required to melt 1 mol of a substance is its enthalpy of fusion (ΔH_{fus}). The energy change required to vaporize 1 mol of a substance is the enthalpy of vaporization (ΔH_{vap}). The direct conversion of a solid to a gas is **sublimation**. The amount of energy needed to sublime 1 mol of a substance is its **enthalpy of sublimation (ΔH_{sub})** and is the sum of the enthalpies of fusion and vaporization. Plots of the temperature of a substance versus heat added or versus heating time at a constant rate of heating are called **heating curves**. Heating curves relate temperature changes to phase transitions. A **superheated liquid**, a liquid at a temperature and pressure at which it should be a gas, is not stable. A **cooling curve** is not exactly the reverse of the heating curve because many liquids do not freeze at the expected temperature. Instead, they form a **supercooled liquid**, a metastable liquid phase that exists below the normal melting point. Supercooled liquids usually crystallize on standing, or adding a **seed crystal** of the same or another substance can induce crystallization.

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3.6: Phase Diagrams

Learning Objectives

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

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

Introduction

A typical phase diagram consists of discrete regions that represent the different phases exhibited by a substance (Figure 3.6.1). Each region corresponds to the range of combinations of temperature and pressure over which that phase is stable. The combination of high pressure and low temperature (upper left of Figure 3.6.1) corresponds to the solid phase, whereas the gas phase is favored at high temperature and low pressure (lower right). The combination of high temperature and high pressure (upper right) corresponds to a supercritical fluid.

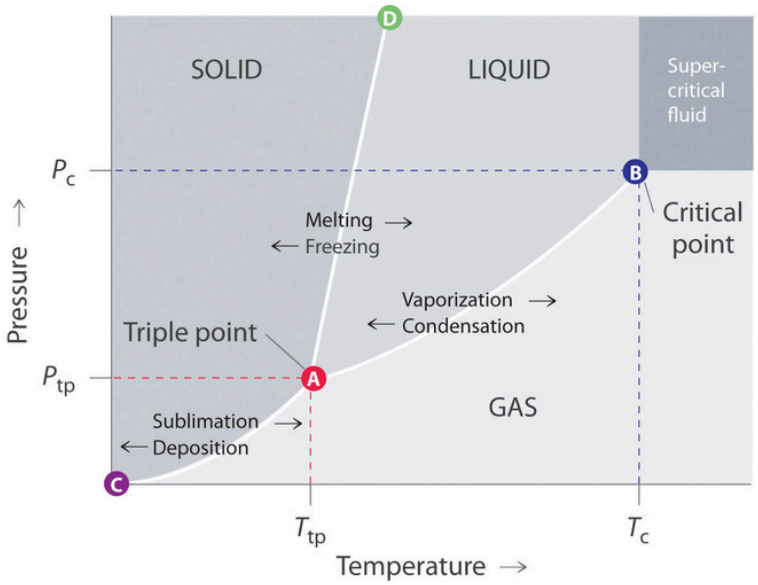


Figure 3.6.1: A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region

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

The lines in a phase diagram correspond to the combinations of temperature and pressure at which two phases can coexist in equilibrium. In Figure 3.6.1, the line that connects points A and D separates the solid and liquid phases and shows how the melting point of a solid varies with pressure. The solid and liquid phases are in equilibrium all along this line; crossing the line horizontally corresponds to melting or freezing. The line that connects points A and B is the vapor pressure curve of the liquid, which we discussed in Section 11.5. It ends at the critical point, beyond which the substance exists as a supercritical fluid. The line that connects points A and C is the vapor pressure curve of the *solid* phase. Along this line, the solid is in equilibrium with the vapor phase through sublimation and deposition. Finally, point A, where the solid/liquid, liquid/gas, and solid/gas lines intersect, is the triple point; it is the *only* combination of temperature and pressure at which all three phases (solid, liquid, and gas) are in

equilibrium and can therefore exist simultaneously. Because no more than three phases can ever coexist, a phase diagram can never have more than three lines intersecting at a single point.

Remember that a phase diagram, such as the one in Figure 3.6.1, is for a single pure substance in a closed system, not for a liquid in an open beaker in contact with air at 1 atm pressure. In practice, however, the conclusions reached about the behavior of a substance in a closed system can usually be extrapolated to an open system without a great deal of error.

The Phase Diagram of Water

Figure 3.6.2 shows the phase diagram of water and illustrates that the triple point of water occurs at 0.01°C and 0.00604 atm (4.59 mmHg). Far more reproducible than the melting point of ice, which depends on the amount of dissolved air and the atmospheric pressure, the triple point (273.16 K) is used to define the absolute (Kelvin) temperature scale. The triple point also represents the lowest pressure at which a liquid phase can exist in equilibrium with the solid or vapor. At pressures less than 0.00604 atm, therefore, ice does not melt to a liquid as the temperature increases; the solid sublimes directly to water vapor. Sublimation of water at low temperature and pressure can be used to "freeze-dry" foods and beverages. The food or beverage is first cooled to subzero temperatures and placed in a container in which the pressure is maintained below 0.00604 atm. Then, as the temperature is increased, the water sublimes, leaving the dehydrated food (such as that used by backpackers or astronauts) or the powdered beverage (as with freeze-dried coffee).

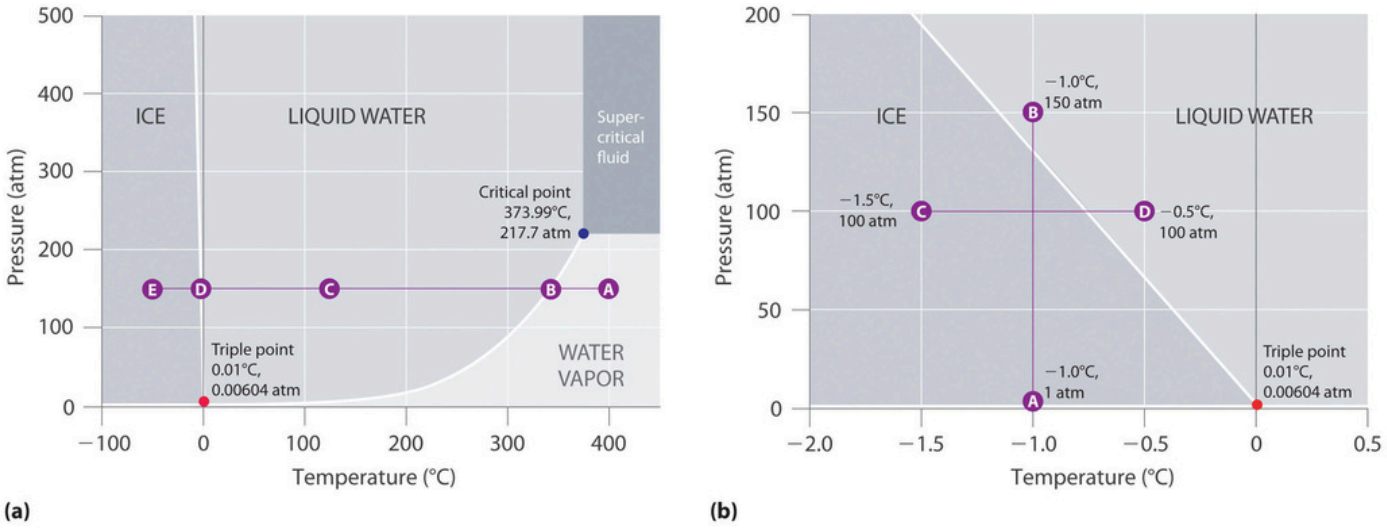


Figure 3.6.2: Two Versions of the Phase Diagram of Water. (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example 3.6.1).

The phase diagram for water illustrated in Figure 3.6.2*b* shows the boundary between ice and water on an expanded scale. The melting curve of ice slopes up and slightly to the left rather than up and to the right as in Figure 3.6.1; that is, the melting point of ice *decreases* with increasing pressure; at 100 MPa (987 atm), ice melts at −9°C. Water behaves this way because it is one of the few known substances for which the crystalline solid is *less dense* than the liquid (others include antimony and bismuth). Increasing the pressure of ice that is in equilibrium with water at 0°C and 1 atm tends to push some of the molecules closer together, thus decreasing the volume of the sample. The decrease in volume (and corresponding increase in density) is smaller for a solid or a liquid than for a gas, but it is sufficient to melt some of the ice.

In Figure 3.6.2*b* point A is located at P = 1 atm and T = −1.0°C, within the solid (ice) region of the phase diagram. As the pressure increases to 150 atm while the temperature remains the same, the line from point A crosses the ice/water boundary to point B, which lies in the liquid water region. Consequently, applying a pressure of 150 atm will melt ice at −1.0°C. We have already indicated that the pressure dependence of the melting point of water is of vital importance. If the solid/liquid boundary in the phase diagram of water were to slant up and to the right rather than to the left, ice would be denser than water, ice cubes would

sink, water pipes would not burst when they freeze, and antifreeze would be unnecessary in automobile engines.

Ice Skating: An Incorrect Hypothesis of Phase Transitions

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



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

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

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

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

$$F = mg$$

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

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

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

$$A = (2.0 \times 10^{-3}\ m)(25 \times 10^{-2}\ m) = 5.0 \times 10^{-4} m^2$$

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

$$P = \frac{736\ N}{5.0 \times 10^{-4}\ m^2} = 1.5 \times 10^6\ N/m^2 = 1.5 \times 10^6\ Pa = 15\ atm$$

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

Example 3.6.1: Water

Referring to the phase diagram of water in Figure 3.6.2:

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

Given: phase diagram, temperature, and pressure

Asked for: physical form and physical changes

Strategy:

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

Solution:

a. **A** Locate the starting point on the phase diagram in part (a) in Figure 3.6.2. The initial conditions correspond to point A, which lies in the region of the phase diagram representing water vapor. Thus water at T = 400°C and P = 150 atm is a gas.
b. **B** Cooling the sample at constant pressure corresponds to moving left along the horizontal line in part (a) in Figure 3.6.2 . At about 340°C (point B), we cross the vapor pressure curve, at which point water vapor will begin to condense and the sample will consist of a mixture of vapor and liquid. When all of the vapor has condensed, the temperature drops further, and we enter the region corresponding to liquid water (indicated by point C). Further cooling brings us to the melting curve, the line that separates the liquid and solid phases at a little below 0°C (point D), at which point the sample will consist of a mixture of liquid and solid water (ice). When all of the water has frozen, cooling the sample to −50°C takes us along the horizontal line to point E, which lies within the region corresponding to solid water. At P = 150 atm and T = −50°C, therefore, the sample is solid ice.

Exercise 3.6.2

Referring to the phase diagram of water in Figure 3.6.2, predict the physical form of a sample of water at −0.0050°C as the pressure is gradually increased from 1.0 mmHg to 218 atm.

Answer

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

The Phase Diagram of Carbon Dioxide

In contrast to the phase diagram of water, the phase diagram of CO_2 (Figure $3.6.3$) has a more typical melting curve, sloping up and to the right. The triple point is –56.6°C and 5.11 atm, which means that liquid CO_2 cannot exist at pressures lower than 5.11 atm. At 1 atm, therefore, solid CO_2 sublimes directly to the vapor while maintaining a temperature of –78.5°C, the normal sublimation temperature. Solid CO_2 is generally known as dry ice because it is a cold solid with no liquid phase observed when it is warmed.



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

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

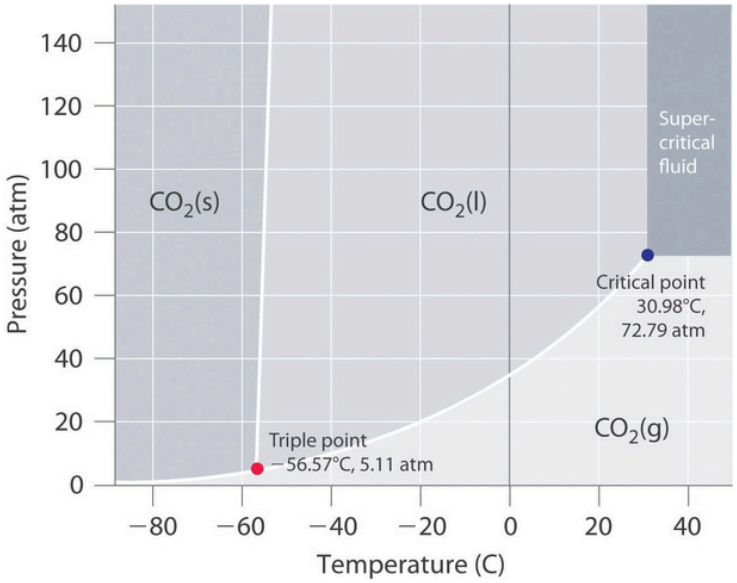


Figure $3.6.3$: The Phase Diagram of Carbon Dioxide. Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

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

The Critical Point

As the phase diagrams above demonstrate, a combination of high pressure and low temperature allows gases to be liquefied. As we increase the temperature of a gas, liquefaction becomes more and more difficult because higher and higher pressures are required to overcome the increased kinetic energy of the molecules. In fact, for every substance, there is some temperature above which the gas can no longer be liquefied, regardless of pressure. This temperature is the critical temperature (T_c), the highest temperature at which a substance can exist as a liquid. Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container. Substances with strong intermolecular forces tend to form a liquid phase over a very large temperature range and therefore have high critical temperatures. Conversely, substances with weak intermolecular interactions have relatively low critical temperatures. Each substance also has a critical pressure (P_c), the minimum pressure needed to liquefy it at the critical temperature. The combination of critical temperature and critical pressure is called the critical point. The critical temperatures and pressures of several common substances are listed in Figure 3.6.1.

Figure 3.6.1: Critical Temperatures and Pressures of Some Simple Substances

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

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

Supercritical Fluids

YouTube Video

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

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3.7: Clausius-Clapeyron Equation

Learning Objectives

- Apply the Clausius-Clapeyron equation to estimate the vapor pressure at any temperature.
- Estimate the heat of phase transition from the vapor pressures measured at two temperatures.

The *vaporization curves* of most liquids have similar shapes with the vapor pressure steadily increasing as the temperature increases (Figure 3.7.1).

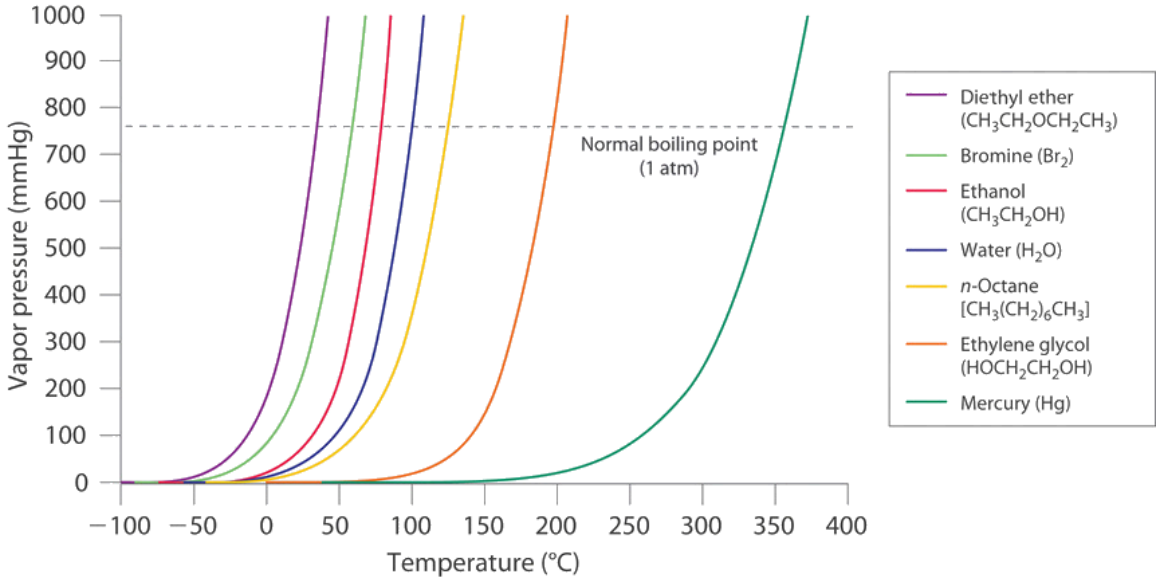


Figure 3.7.1: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the *P* = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC 3.0; Anonymous)

A good approach is to find a mathematical model for the pressure increase as a function of temperature. Experiments showed that the vapor pressure P and temperature T are related,

[redacted]

where ΔH_{vap} is the Enthalpy (heat) of Vaporization and R is the gas constant (8.3145 J mol^{-1} K^{-1}).

A simple relationship can be found by integrating Equation 3.4.140 between two pressure-temperature endpoints:

[redacted]

where P_1 and P_2 are the vapor pressures at two temperatures T_1 and T_2. Equation 3.4.143 is known as the **Clausius-Clapeyron Equation** and allows us to estimate the vapor pressure at another temperature, if the vapor pressure is known at some temperature, and if the enthalpy of vaporization is known.

Alternative Formulation

The order of the temperatures in Equation 3.4.143 matters as the Clausius-Clapeyron Equation is sometimes written with a negative sign (and switched order of temperatures):

[redacted]

Example 3.7.1: Vapor Pressure of Water

The vapor pressure of water is 1.0 atm at 373 K, and the enthalpy of vaporization is 40.7 kJ mol^{-1}. Estimate the vapor pressure at temperature 363 and 383 K respectively.

Solution

Using the Clausius-Clapeyron equation (Equation 3.7.1072), we have:

$$\begin{aligned} P_{363} &= 1.0 \exp\left[-\left(\frac{40,700}{8.3145}\right)\left(\frac{1}{363\ K}-\frac{1}{373\ K}\right)\right] \\ &= 0.697 \text{ atm} \end{aligned}$$

$$\begin{aligned} P_{383} &= 1.0 \exp\left[-\left(\frac{40,700}{8.3145}\right)\left(\frac{1}{383\ K}-\frac{1}{373\ K}\right)\right] \\ &= 1.409 \text{ atm} \end{aligned}$$

Note that the increase in vapor pressure from 363 K to 373 K is 0.303 atm, but the increase from 373 to 383 K is 0.409 atm. The increase in vapor pressure is not a linear process.

Discussion

We can use the Clausius-Clapeyron equation to construct the entire vaporization curve. There is a deviation from experimental value, that is because the enthalpy of vaporization varies slightly with temperature.

The Clausius-Clapeyron equation can be also applied to sublimation; the following example shows its application in estimating the heat of sublimation.

Example 3.7.2: Sublimation of Ice

The vapor pressures of ice at 268 K and 273 K are 2.965 and 4.560 torr respectively. Estimate the heat of sublimation of ice.

Solution

The enthalpy of sublimation is ΔH_{sub}. Use a piece of paper and derive the Clausius-Clapeyron equation so that you can get the form:

$$\begin{aligned} \Delta H_{sub} &= \frac{R \ln\left(\frac{P_{273}}{P_{268}}\right)}{\frac{1}{268\ K}-\frac{1}{273\ K}} \\ &= \frac{8.3145 \ln\left(\frac{4.560}{2.965}\right)}{\frac{1}{268\ \text{K}}-\frac{1}{273\ \text{K}}} \\ &= 52,370 \text{ J mol}^{-1} \end{aligned}$$

Note that the heat of sublimation is the sum of heat of melting (6,006 J/mol at 0°C and 101 kPa) and the heat of vaporization (45,051 J/mol at 0 °C).

Exercise 3.7.2

Show that the vapor pressure of ice at 274 K is higher than that of water at the same temperature. Note the curve of vaporization is also called the curve of vaporization.

Example 3.7.3: Vaporization of Ethanol

Calculate ΔH_{vap} for ethanol, given vapor pressure at 40 °C = 150 torr. The normal boiling point for ethanol is 78 °C.

Solution

Recognize that we have TWO sets of (P, T) data:

- Set 1: (150 torr at 40+273K)
- Set 2: (760 torr at 78+273K)

We then directly use these data in Equation 3.7.1072

$$\ln\left(\frac{150}{760}\right) = \frac{-\Delta H_{vap}}{8.314}\left[\frac{1}{313} - \frac{1}{351}\right]$$

$$\ln 150 - \ln 760 = \frac{-\Delta H_{vap}}{8.314}\left[\frac{1}{313} - \frac{1}{351}\right]$$

$$-1.623 = \frac{-\Delta H_{vap}}{8.314}\left[0.0032 - 0.0028\right]$$

Then solving for ΔH_{vap}

$$\begin{aligned}\Delta H_{vap} &= 3.90 \times 10^4 \text{ J/mol} \\ &= 39.0 \text{ kJ/mol}\end{aligned}$$

Advanced Note

It is important to not use the Clausius-Clapeyron equation for the solid to liquid transition. That requires the use of the more general **Clapeyron equation**

$$\frac{dP}{dT} = \frac{\Delta \bar{H}}{T\Delta \bar{V}}$$

where $\Delta \bar{H}$ and $\Delta \bar{V}$ is the molar change in enthalpy (the enthalpy of fusion in this case) and volume respectively between the two phases in the transition.

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3.8: The Solid State

Learning Objectives

- Define and describe the bonding and properties of ionic, molecular, metallic, and covalent network crystalline solids
- Describe the main types of crystalline solids: ionic solids, metallic solids, covalent network solids, and molecular solids
- Explain the ways in which crystal defects can occur in a solid

When most liquids are cooled, they eventually freeze and form crystalline solids, solids in which the atoms, ions, or molecules are arranged in a definite repeating pattern. It is also possible for a liquid to freeze before its molecules become arranged in an orderly pattern. The resulting materials are called amorphous solids or noncrystalline solids (or, sometimes, glasses). The particles of such solids lack an ordered internal structure and are randomly arranged (Figure 3.8.1).

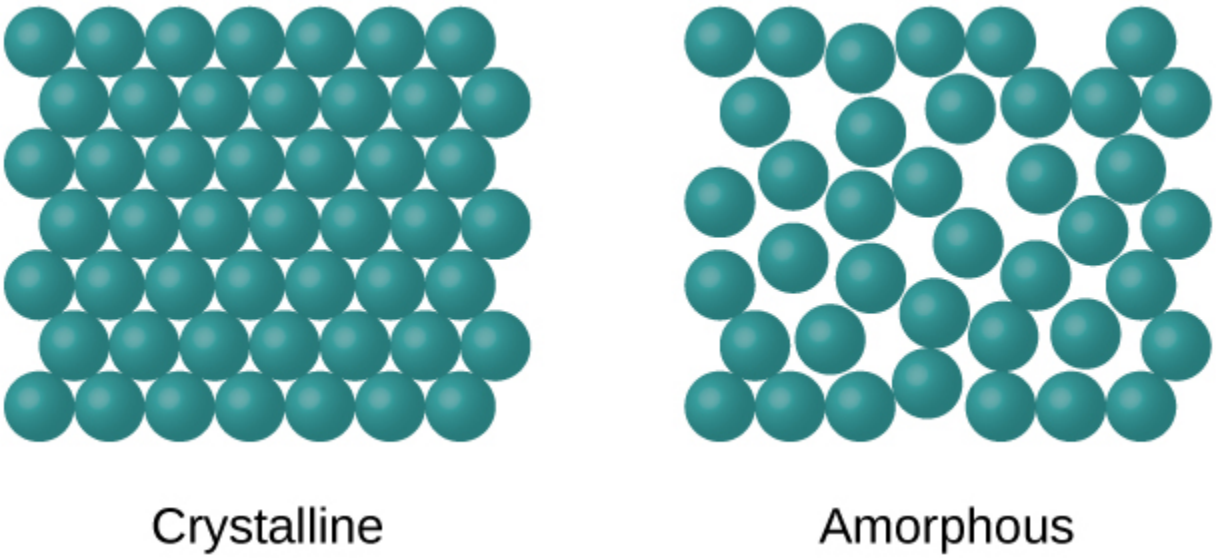


Figure 3.8.1: The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous).

The crystalline arrangement shows many circles drawn in rows and stacked together tightly. The amorphous arrangement shows many circles spread slightly apart and in no organized pattern.

Metals and ionic compounds typically form ordered, crystalline solids. Substances that consist of large molecules, or a mixture of molecules whose movements are more restricted, often form amorphous solids. For examples, candle waxes are amorphous solids composed of large hydrocarbon molecules. Some substances, such as boron oxide (Figure 3.8.2), can form either crystalline or amorphous solids, depending on the conditions under which it is produced. Also, amorphous solids may undergo a transition to the crystalline state under appropriate conditions.

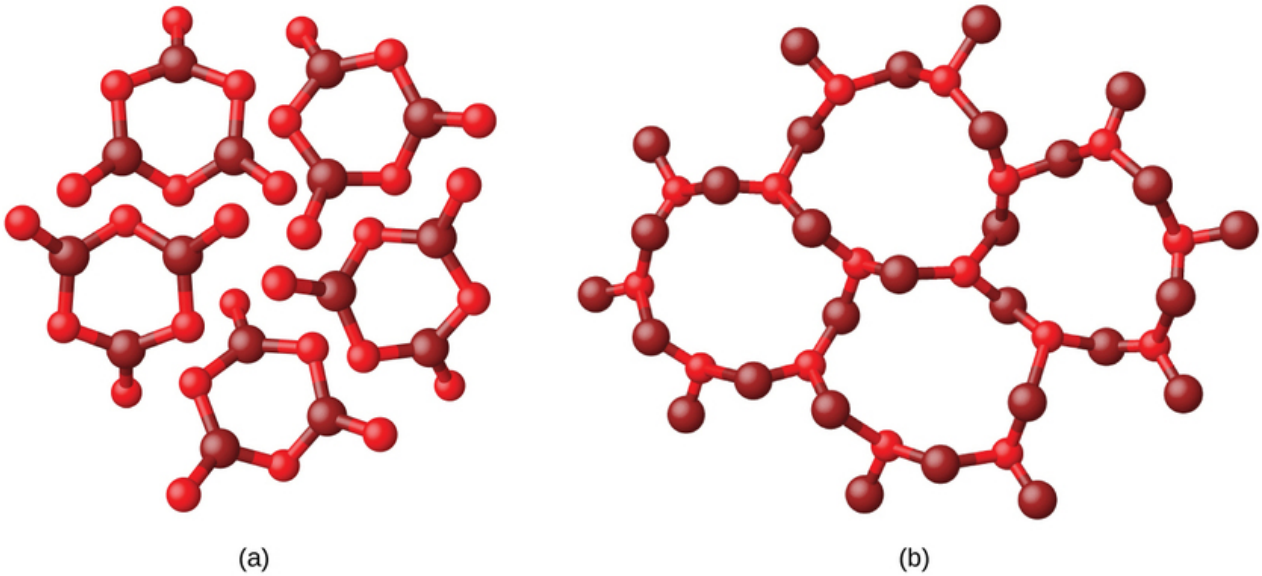


Figure 3.8.2: (a) Diboron trioxide, B_2O_3, is normally found as a white, amorphous solid (a glass), which has a high degree of disorder in its structure. (b) By careful, extended heating, it can be converted into a crystalline form of B_2O_3, which has a very ordered arrangement.

The first structure of diboron trioxide shows five identical and separated hexagonal rings. The second structure of diboron trioxide shows a more interconnected structure with four large rings forming a more stable structure.

Crystalline solids are generally classified according the nature of the forces that hold its particles together. These forces are primarily responsible for the physical properties exhibited by the bulk solids. The following sections provide descriptions of the major types of crystalline solids: ionic, metallic, covalent network, and molecular.

Ionic Solids

Ionic solids, such as sodium chloride and nickel oxide, are composed of positive and negative ions that are held together by electrostatic attractions, which can be quite strong (Figure 3.8.3). Many ionic crystals also have high melting points. This is due to the very strong attractions between the ions—in ionic compounds, the attractions between full charges are (much) larger than those between the partial charges in polar molecular compounds. This will be looked at in more detail in a later discussion of lattice energies. Although they are hard, they also tend to be brittle, and they shatter rather than bend. Ionic solids do not conduct electricity; however, they do conduct when molten or dissolved because their ions are free to move. Many simple compounds formed by the reaction of a metallic element with a nonmetallic element are ionic.

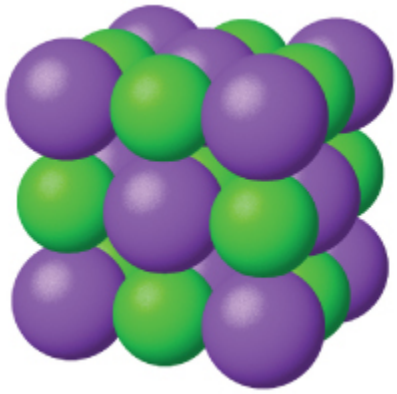


Figure 3.8.3: Sodium chloride is an ionic solid.

A cube composed of purple and green spheres is shown. The cube has dimensions of three by three spheres. The purple spheres are slightly larger than the green spheres.

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure 3.8.4. The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a “sea” of delocalized electrons. The atoms within such a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials. The melting points of the metals vary widely. Mercury is a liquid at room temperature, and the alkali metals melt below 200 °C. Several post-transition metals also have low melting points, whereas the transition metals melt at temperatures above 1000 °C. These differences reflect differences in strengths of metallic bonding among the metals.

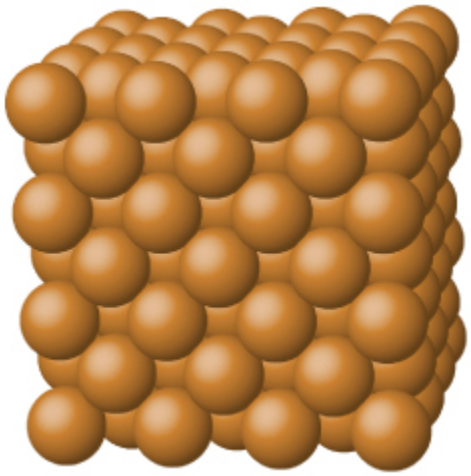


Figure 3.8.4: Copper is a metallic solid.

Covalent Network Solids

Covalent network solids include crystals of diamond, silicon, some other nonmetals, and some covalent compounds such as silicon dioxide (sand) and silicon carbide (carborundum, the abrasive on sandpaper). Many minerals have networks of covalent bonds. The atoms in these solids are held together by a network of covalent bonds, as shown in Figure 3.8.5. To break or to melt a covalent network solid, covalent bonds must be broken. Because covalent bonds are relatively strong, covalent network solids are typically characterized by hardness, strength, and high melting points. For example, diamond is one of the hardest substances known and melts above 3500 °C.

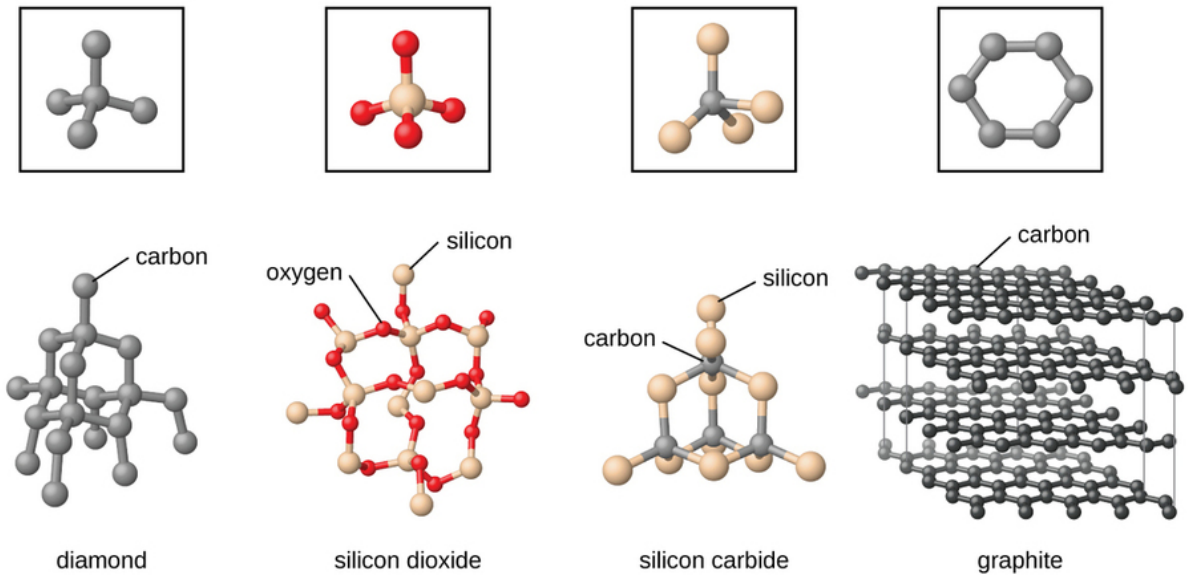


Figure 3.8.5. A covalent crystal contains a three-dimensional network of covalent bonds, as illustrated by the structures of diamond, silicon dioxide, silicon carbide, and graphite. Graphite is an exceptional example, composed of planar sheets of covalent crystals that are held together in layers by noncovalent forces. Unlike typical covalent solids, graphite is very soft and electrically conductive.

The complex three dimensional structure of diamond, silicon dioxide, silicon carbide and graphite is shown along with a a smaller repeating unit of the structure shown above each structure.

Molecular Solids

Molecular solids, such as ice, sucrose (table sugar), and iodine, as shown in Figure 3.8.6, are composed of neutral molecules. The strengths of the attractive forces between the units present in different crystals vary widely, as indicated by the melting points of the crystals. Small symmetrical molecules (nonpolar molecules), such as H_2, N_2, O_2, and F_2, have weak attractive forces and form molecular solids with very low melting points (below –200 °C). Substances consisting of larger, nonpolar molecules have larger attractive forces and melt at higher temperatures. Molecular solids composed of molecules with permanent dipole moments (polar molecules) melt at still higher temperatures. Examples include ice (melting point, 0 °C) and table sugar (melting point, 185 °C).

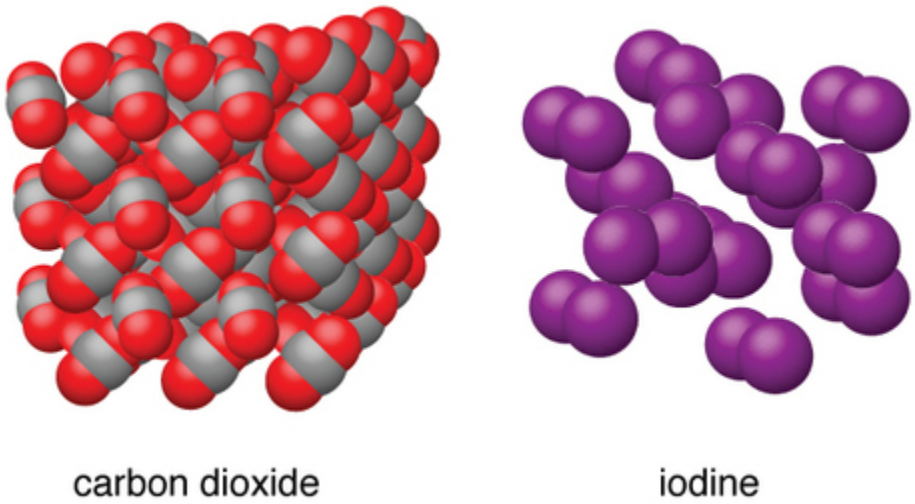


Figure 3.8.6: Carbon dioxide (CO_2) consists of small, nonpolar molecules and forms a molecular solid with a melting point of –78 °C. Iodine (I_2) consists of larger, nonpolar molecules and forms a molecular solid that melts at 114 °C.

On the left, many red and grey molecules are densely stacked in a 3-D drawing to represent carbon dioxide. On the right, purple molecules are scattered randomly to represent iodine.

Properties of Solids

A crystalline solid, like those listed in Table 3.8.1 has a precise melting temperature because each atom or molecule of the same type is held in place with the same forces or energy. Thus, the attractions between the units that make up the crystal all have the same strength and all require the same amount of energy to be broken. The gradual softening of an amorphous material differs dramatically from the distinct melting of a crystalline solid. This results from the structural nonequivalence of the molecules in the amorphous solid. Some forces are weaker than others, and when an amorphous material is heated, the weakest intermolecular attractions break first. As the temperature is increased further, the stronger attractions are broken. Thus amorphous materials soften over a range of temperatures.

Table 3.8.1: Types of Crystalline Solids and Their Properties

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
ionic	ions	ionic bonds	hard, brittle, conducts electricity as a liquid but not as a solid, high to very high melting points	NaCl, Al_2O_3
metallic	atoms of electropositive elements	metallic bonds	shiny, malleable, ductile, conducts heat and electricity well, variable hardness and melting temperature	Cu, Fe, Ti, Pb, U
covalent network	atoms of electronegative elements	covalent bonds	very hard, not conductive, very high melting points	C (diamond), SiO_2, SiC
molecular	molecules (or atoms)	IMFs	variable hardness, variable brittleness, not conductive, low melting points	H_2O, CO_2, I_2, $C_{12}H_{22}O_{11}$

Graphene: Material of the Future

Carbon is an essential element in our world. The unique properties of carbon atoms allow the existence of carbon-based life forms such as ourselves. Carbon forms a huge variety of substances that we use on a daily basis, including those shown in Figure 3.8.7. You may be familiar with diamond and graphite, the two most common *allotropes* of carbon. (Allotropes are different structural forms of the same element.) Diamond is one of the hardest-known substances, whereas graphite is soft enough to be used as pencil lead. These very different properties stem from the different arrangements of the carbon atoms in the different allotropes.

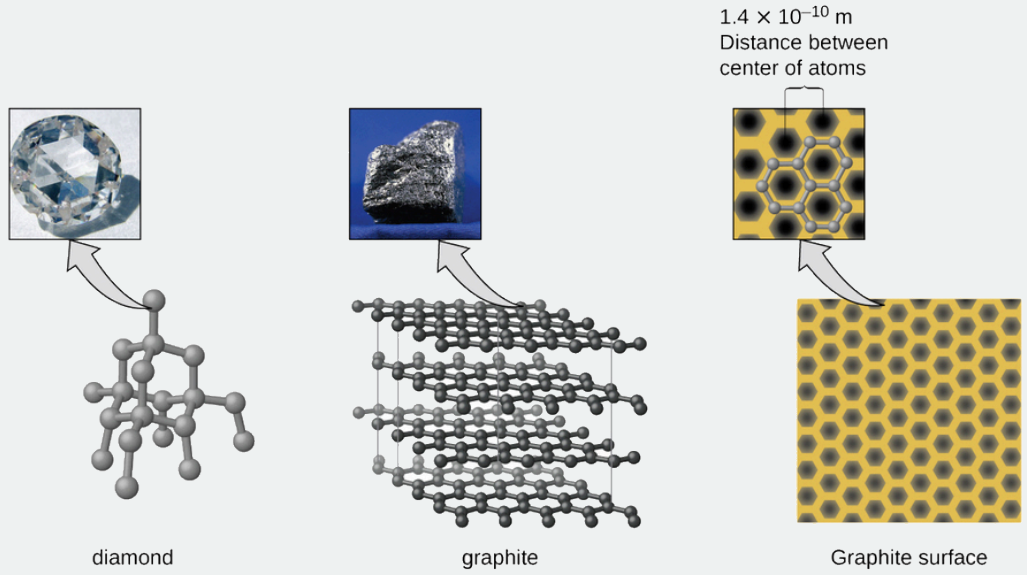


Figure 3.8.7: Diamond is extremely hard because of the strong bonding between carbon atoms in all directions. Graphite (in pencil lead) rubs off onto paper due to the weak attractions between the carbon layers. An image of a graphite surface shows the distance between the centers of adjacent carbon atoms. (credit left photo: modification of work by Steve Jurvetson; credit middle photo: modification of work by United States Geological Survey)

A close up of a piece of diamond shows a three dimensional sturcture of a complex network of well bonded carbon atoms. A close up of a graphite shows several layers of carbon sheets. Each sheet is composed of a repeated and connected hexagonal structure of carbon atoms. The third diagram shows that the distance between the center of atoms is 1.4 times 10 to the power of negative 10 meters.

You may be less familiar with a recently discovered form of carbon: graphene. Graphene was first isolated in 2004 by using tape to peel off thinner and thinner layers from graphite. It is essentially a single sheet (one atom thick) of graphite. Graphene, illustrated in Figure 3.8.8, is not only strong and lightweight, but it is also an excellent conductor of electricity and heat. These properties may prove very useful in a wide range of applications, such as vastly improved computer chips and circuits, better batteries and solar cells, and stronger and lighter structural materials. The 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov for their pioneering work with graphene.

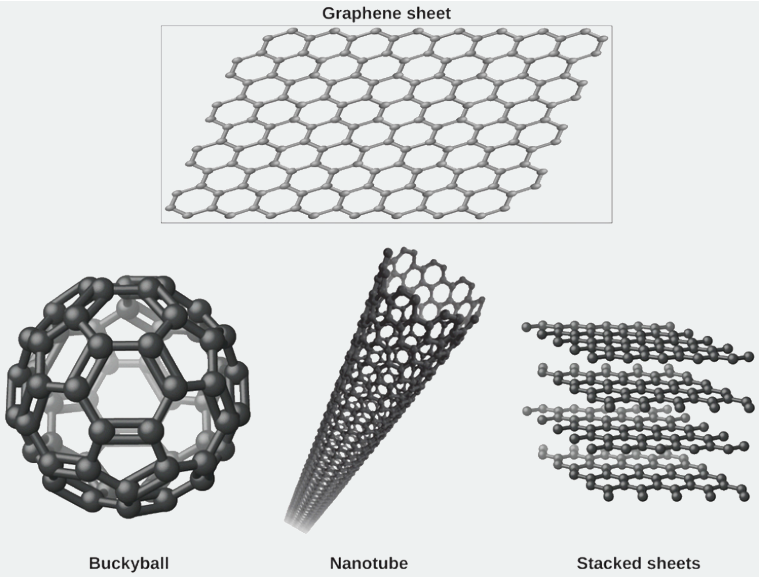


Figure 3.8.8: Graphene sheets can be formed into buckyballs, nanotubes, and stacked layers.

A sheet of interconnected hexagonal rings is shown at the top. Below it, a bukcyball is shown which is a sphere is composed of hexagonal rings. In the lower middle image, a nanotube is shown that is made by rolling a graphene sheet into a tube. In the lower right image, stacked sheets made up of four horizontal sheets composed of joined, hexagonal rings is shown.

Crystal Defects

In a crystalline solid, the atoms, ions, or molecules are arranged in a definite repeating pattern, but occasional defects may occur in the pattern. Several types of defects are known, as illustrated in Figure 3.8.9. Vacancies are defects that occur when positions that should contain atoms or ions are vacant. Less commonly, some atoms or ions in a crystal may occupy positions, called interstitial sites, located between the regular positions for atoms. Other distortions are found in impure crystals, as, for example, when the cations, anions, or molecules of the impurity are too large to fit into the regular positions without distorting the structure. Trace amounts of impurities are sometimes added to a crystal (a process known as *doping)* in order to create defects in the structure that yield desirable changes in its properties. For example, silicon crystals are doped with varying amounts of different elements to yield suitable electrical properties for their use in the manufacture of semiconductors and computer chips.

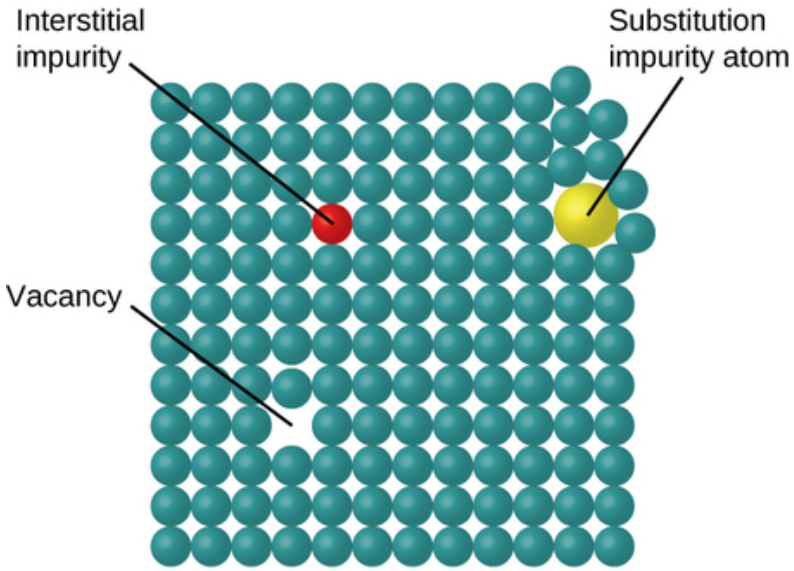


Figure 3.8.9: Types of crystal defects include vacancies, interstitial atoms, and substitutions impurities.

Summary

Some substances form crystalline solids consisting of particles in a very organized structure; others form amorphous (noncrystalline) solids with an internal structure that is not ordered. The main types of crystalline solids are ionic solids, metallic solids, covalent network solids, and molecular solids. The properties of the different kinds of crystalline solids are due to the types of particles of which they consist, the arrangements of the particles, and the strengths of the attractions between them. Because their particles experience identical attractions, crystalline solids have distinct melting temperatures; the particles in amorphous solids experience a range of interactions, so they soften gradually and melt over a range of temperatures. Some crystalline solids have defects in the definite repeating pattern of their particles. These defects (which include vacancies, atoms or ions not in the regular positions, and impurities) change physical properties such as electrical conductivity, which is exploited in the silicon crystals used to manufacture computer chips.

Glossary

amorphous solid
: (also, noncrystalline solid) solid in which the particles lack an ordered internal structure

covalent network solid
: solid whose particles are held together by covalent bonds

crystalline solid
: solid in which the particles are arranged in a definite repeating pattern

interstitial sites
: spaces between the regular particle positions in any array of atoms or ions

ionic solid
: solid composed of positive and negative ions held together by strong electrostatic attractions

metallic solid
: solid composed of metal atoms

molecular solid
: solid composed of neutral molecules held together by intermolecular forces of attraction

vacancy
: defect that occurs when a position that should contain an atom or ion is vacant

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3.9: Bonding in Metals

In the early 1900's, Paul Drüde came up with the "sea of electrons" metallic bonding theory by modeling metals as a mixture of atomic cores (atomic cores = positive nuclei + inner shell of electrons) and valence electrons. Metallic bonds occur among metal atoms. Whereas ionic bonds join metals to non-metals, *metallic bonding joins a bulk of metal atoms*. A sheet of aluminum foil and a copper wire are both places where you can see metallic bonding in action.

Metals tend to have high melting points and boiling points suggesting strong bonds between the atoms. Even a soft metal like sodium (melting point 97.8°C) melts at a considerably higher temperature than the element (neon) which precedes it in the Periodic Table. Sodium has the electronic structure $1s^2 2s^2 2p^6 3s^1$. When sodium atoms come together, the electron in the 3s atomic orbital of one sodium atom shares space with the corresponding electron on a neighboring atom to form a molecular orbital - in much the same sort of way that a covalent bond is formed.

The difference, however, is that each sodium atom is being touched by eight other sodium atoms - and the sharing occurs between the central atom and the 3s orbitals on all of the eight other atoms. Each of these eight is in turn being touched by eight sodium atoms, which in turn are touched by eight atoms - and so on and so on, until you have taken in all the atoms in that lump of sodium. *All* of the 3s orbitals on all of the atoms overlap to give a vast number of molecular orbitals that extend over the whole piece of metal. There have to be huge numbers of molecular orbitals, of course, because any orbital can only hold two electrons.

The electrons can move freely within these molecular orbitals, and so each electron becomes detached from its parent atom. The electrons are said to be delocalized. The metal is held together by the strong forces of attraction between the positive nuclei and the delocalized electrons (Figure $3.9.1$).

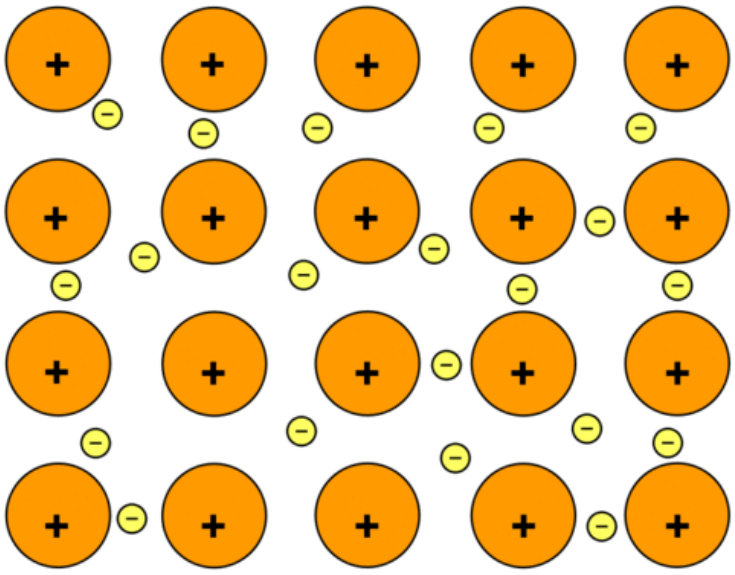


Figure $3.9.1$: Metallic Bonding: The Electron Sea Model: Positive atomic nuclei (orange circles) surrounded by a sea of delocalized electrons (yellow circles).

This is sometimes described as "an array of positive ions in a sea of electrons". If you are going to use this view, beware! Is a metal made up of atoms or ions? It is made of atoms**.** Each positive center in the diagram represents all the rest of the atom apart from the outer electron, but that electron has not been lost - it may no longer have an attachment to a particular atom, but it's still there in the structure. Sodium metal is therefore written as Na, not $\mathrm{Na^+}$.

Example 3.9.1: Metallic bonding in magnesium

Use the sea of electrons model to explain why Magnesium has a higher melting point (650 °C) than sodium (97.79 °C).

Solution

If you work through the same argument above for sodium with magnesium, you end up with stronger bonds and hence a higher melting point.

Magnesium has the outer electronic structure $3s^2$. Both of these electrons become delocalized, so the "sea" has twice the electron density as it does in sodium. The remaining "ions" also have twice the charge (if you are going to use this particular view of the metal bond) and so there will be more attraction between "ions" and "sea".

More realistically, each magnesium atom has 12 protons in the nucleus compared with sodium's 11. In both cases, the nucleus is screened from the delocalized electrons by the same number of inner electrons - the 10 electrons in the $1s^2$ $2s^2$ $2p^6$ orbitals. That means that there will be a net pull from the magnesium nucleus of 2+, but only 1+ from the sodium nucleus.

So not only will there be a greater number of delocalized electrons in magnesium, but there will also be a greater attraction for them from the magnesium nuclei. Magnesium atoms also have a slightly smaller radius than sodium atoms, and so the delocalized electrons are closer to the nuclei. Each magnesium atom also has twelve near neighbors rather than sodium's eight. Both of these factors increase the strength of the bond still further.

Note: Transition metals tend to have particularly high melting points and boiling points. The reason is that they can involve the 3d electrons in the delocalization as well as the 4s. The more electrons you can involve, the stronger the attractions tend to be.

Bulk properties of metals

Metals have several qualities that are unique, such as the ability to conduct electricity and heat, a low ionization energy, and a low electronegativity (so they will give up electrons easily to form cations). Their physical properties include a lustrous (shiny) appearance, and they are malleable and ductile. Metals have a crystal structure but can be easily deformed. In this model, the valence electrons are free, delocalized, mobile, and not associated with any particular atom. This model may account for:

- **Conductivity**: Since the electrons are free, if electrons from an outside source were pushed into a metal wire at one end (Figure 3.9.2), the electrons would move through the wire and come out at the other end at the same rate (conductivity is the movement of charge).

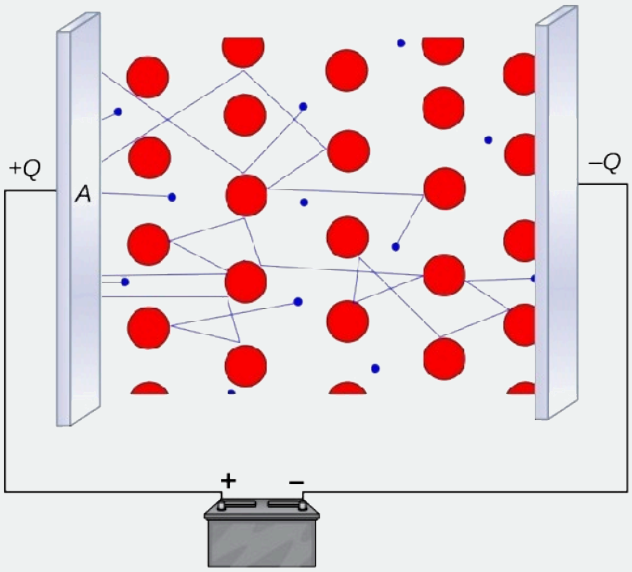


Figure 3.9.2: The "sea of electrons" is free to flow about the crystal of positive metal ions. These flowing electron can conduct electrical change when an electric field is applied (e.g., a battery). (CC-BY-SA; OpenStax and Rafaelgarcia).

- **Malleability** and **Ductility**: The electron-sea model of metals not only explains their electrical properties but their malleability and ductility as well. The sea of electrons surrounding the protons acts like a cushion, and so when the metal is hammered on, for instance, the overall composition of the structure of the metal is not harmed or changed. The protons may be rearranged but the sea of electrons with adjust to the new formation of protons and keep the metal intact. When one layer of ions in an electron sea moves along one space with respect to the layer below it, the crystal structure does not fracture but is only deformed (Figure 3.9.3).



Figure 3.9.3: Malleability of metals originate from each of moving layer of atoms with respect to each other. The final situation is much the same as the initial. Thus if we hit a metal with a hammer, the crystals do not shatter, but merely change their shape, This is very different from the behavior of ionic crystals.

- **Heat capacity**: This is explained by the ability of free electrons to move about the solid.
- **Luster**: The free electrons can absorb photons in the "sea," so metals are opaque-looking. Electrons on the surface can bounce back light at the same frequency that the light hits the surface, therefore the metal appears to be shiny.

However, these observations are only qualitative, and not quantitative, so they cannot be tested. The "Sea of Electrons" theory stands today only as an oversimplified model of how metallic bonding works.

In a molten metal, the metallic bond is still present, although the ordered structure has been broken down. The metallic bond is not fully broken until the metal boils. That means that boiling point is actually a better guide to the strength of the metallic bond than melting point is. On melting, the bond is loosened, not broken. The strength of a metallic bond depends on three things:

1. The number of electrons that become delocalized from the metal
2. The charge of the cation (metal).
3. The size of the cation.

A **strong** metallic bond will be the result of more delocalized electrons, which causes the effective nuclear charge on electrons on the cation to increase, in effect making the size of the cation smaller. Metallic bonds are strong and require a great deal of energy to break, and therefore **metals have high melting and boiling points.** A metallic bonding theory must explain how so much bonding can occur with such few electrons (since metals are located on the left side of the periodic table and do not have many electrons in their valence shells). The theory must also account for all of a metal's unique chemical and physical properties.

Expanding the Range of Bonding Possible

Previously, we argued that bonding between atoms can classified as range of possible bonding between **ionic bonds** (fully charge transfer) and **covalent bonds** (fully shared electrons). When two atoms of slightly differing electronegativities come together to form a covalent bond, one atom attracts the electrons more than the other; this is called a polar covalent bond. However, simple "ionic" and "covalent" bonding are idealized concepts and most bonds exist on a two-dimensional continuum described by the van Arkel-Ketelaar Triangle (Figure 3.9.4).

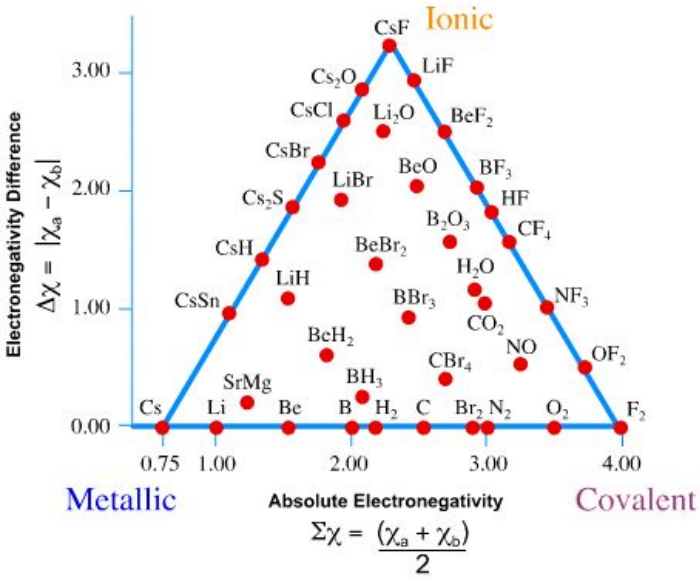


Figure 3.9.4: van Arkel-Ketelaar Triangle plots the difference in electronegativity ($\Delta\chi$) and the average electronegativity in a bond ($\sum\chi$). the top region is where bonds are mostly ionic, the lower left region is where bonding is metallic, and the lower right region is where the bonding is covalent.

Bond triangles or **van Arkel–Ketelaar** triangles (named after Anton Eduard van Arkel and J. A. A. Ketelaar) are triangles used for showing different compounds in varying degrees of ionic, metallic and covalent bonding. In 1941 van Arkel recognized three extreme materials and associated bonding types. Using 36 main group elements, such as metals, metalloids and non-metals, he placed ionic, metallic and covalent bonds on the corners of an equilateral triangle, as well as suggested intermediate species. The bond triangle shows that chemical bonds are not just particular bonds of a specific type. Rather, bond types are interconnected and different compounds have varying degrees of different bonding character (for example, polar covalent bonds).

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

https://www.youtube.com/embed/ZNGThjz82Xo?vq=hd1080

Video 3.9.1: What is the van Arkel-Ketelaar Triangle of Bonding?

Using electronegativity - two compound average electronegativity on x-axis of Figure 3.9.4.

[redacted]

and electronegativity difference on y-axis,

[redacted]

we can rate the dominant bond between the compounds. On the right side of Figure 3.9.4 (from ionic to covalent) should be compounds with varying difference in electronegativity. The compounds with equal electronegativity, such as Cl_2 (chlorine) are placed in the covalent corner, while the ionic corner has compounds with large electronegativity difference, such as $NaCl$ (table salt). The bottom side (from metallic to covalent) contains compounds with varying degree of directionality in the bond. At one extreme is metallic bonds with delocalized bonding and at the other are covalent bonds in which the orbitals overlap in a particular direction. The left side (from ionic to metallic) is meant for delocalized bonds with varying electronegativity difference.

The Three Extremes in bonding

In general:

- Metallic bonds have low $\Delta\chi$ **and** low average $\sum\chi$.
- Ionic bonds have moderate-to-high $\Delta\chi$ and moderate values of average $\sum\chi$.
- Covalent bonds have moderate to high average $\sum\chi$ and can exist with moderately low $\Delta\chi$.

Example 3.9.2

Use the tables of electronegativities (Table A2) and Figure 3.9.4 to estimate the following values

- difference in electronegativity ($\Delta\chi$)
- average electronegativity in a bond ($\sum\chi$)
- percent ionic character
- likely bond type

for the selected compounds:

a. AsH (e.g., in arsine AsH)
b. SrLi
c. KF.

Solution

a: AsH

- The electronegativity of As is 2.18
- The electronegativity of H is 2.22

Using Equations 3.11.232 and 3.9.1073:

$$\begin{aligned}\sum\chi &= \frac{\chi_A + \chi_B}{2} \\ &= \frac{2.18 + 2.22}{2} \\ &= 2.2\end{aligned}$$

$$\begin{aligned}\Delta\chi &= \chi_A - \chi_B \\ &= 2.18 - 2.22 \\ &= 0.04\end{aligned}$$

- From Figure 3.9.4, the bond is fairly nonpolar and has a low ionic character (10% or less)
- The bonding is in the middle of a covalent bond and a metallic bond

b: SrLi

- The electronegativity of Sr is 0.95
- The electronegativity of Li is 0.98

Using Equations 3.11.232 and 3.9.1073:

$$\begin{aligned}\sum\chi &= \frac{\chi_A + \chi_B}{2} \\ &= \frac{0.95 + 0.98}{2} \\ &= 0.965\end{aligned}$$

$$\begin{aligned}\Delta\chi &= \chi_A - \chi_B \\ &= 0.98 - 0.95 \\ &= 0.025\end{aligned}$$

- From Figure 3.9.4, the bond is fairly nonpolar and has a low ionic character (~3% or less)
- The bonding is likely metallic.

c: KF

- The electronegativity of K is 0.82
- The electronegativity of F is 3.98

Using Equations 3.11.232 and 3.9.1073:

$$\begin{aligned}\sum\chi &= \frac{\chi_A + \chi_B}{2} \\ &= \frac{0.82 + 3.98}{2} \\ &= 2.4\end{aligned}$$

$$\begin{aligned}\Delta\chi &= \chi_A - \chi_B \\ &= |0.82 - 3.98| \\ &= 3.16\end{aligned}$$

- From Figure $3.9.4$, the bond is fairly polar and has a high ionic character (~75%)
- The bonding is likely ionic.

Exercise $3.9.2$

Contrast the bonding of NaCl and silicon tetrafluoride.

Answer

NaCl is an ionic crystal structure, and an electrolyte when dissolved in water; $\Delta\chi = 1.58$, average $\sum\chi = 1.79$, while silicon tetrafluoride is covalent (molecular, non-polar gas; $\Delta\chi = 2.08$, average $\sum\chi = 2.94$.

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

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

Q.1

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

Solution

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

Q.3

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

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

Solution

We need to compute the density of the liquid first:

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

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

Calculate the molar volume by:

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

Q.6A

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

Solution

Temperature change = 15^oC

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

Hence, change percentage per ^oC is

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

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

Q.6B

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

Solution

Charles' Law - Ideal Gases

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

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

The material is a non-ideal gas.

Q.7

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

Solution

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

Q.9

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

Solution

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

Q.11

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

the phenomena.

Solution

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

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

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

Q.15

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

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

Solution

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

Q.17

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

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

Solution

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

Q.19

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

Solution

- $\mathrm{He_2} \approx 2.7\mathring{A}$
- $\mathrm{Ar_2} \approx 3.8\mathring{A}$
- $\mathrm{Xe_2} \approx 4.5\mathring{A}$

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

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

Q.23

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

a. $\mathrm{CH_3CH_2CH_2CH_2CH_3}$
b. $\mathrm{CH_3CH_2CH_2CH_2OH}$
c. $\mathrm{CH_4}$
d. $\mathrm{CH_3CH(CH_3)CH_2CH_3}$

Solution

$$\mathrm{CH_3CH_2CH_2CH_2OH} > \mathrm{CH_3CH_2CH_2CH_2CH_3} > \mathrm{CH_3CH(CH_3)CH_2CH_3} > \mathrm{CH_4}$$

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

Q.24

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

Solution

The primary intermolecular forces in the compounds are

- HF → Hydrogen Bonding
- Ar → Dispersion Forces
- CsCl → Ionic Bonding
- HCl → Dipole-Dipole Interactions

Ionic Bonding > Hydrogen Bonding > Dipole-Dipole Interactions > Dispersion Forces

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

Hence the beakers contain

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

Q.25

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

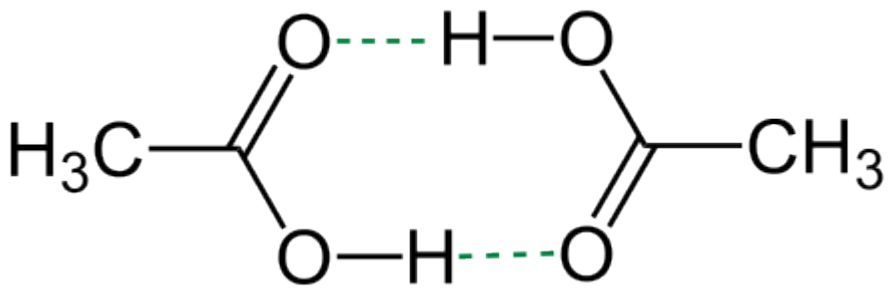
Solution

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

Q.25

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

Solution

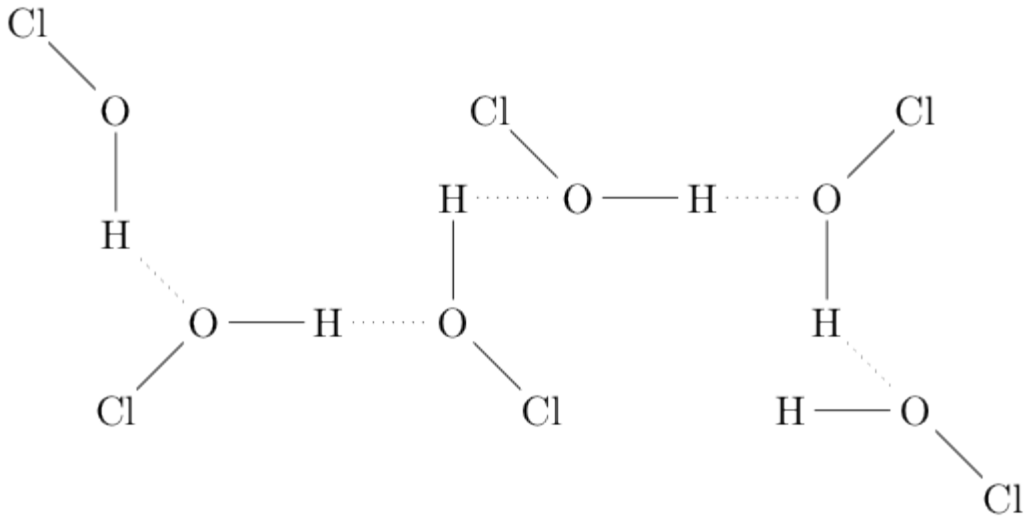


The diagram above shows a reasonable structure of a acetic acid dimer, where the dash lines represent hydrogen bonds.

Q.26

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

Solution



Q.27

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

Solution

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

Q.31

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

Solution

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

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

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

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

Standard pressure = 1 atm

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

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

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

Q.35

Consider the reaction at 25°C.

$$\mathrm{CaC_2\,(s) + 2\,H_2O\,(l) \longrightarrow C_2H_2\,(g) + Ca(OH)_2\,(s)}$$

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

Solution

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

- $P_T = 0.9124atm$
- $P_{\mathrm{H_2O}} = 0.0313atm$

$$P_T - P_{\mathrm{H_2O}} = P_{\mathrm{C_2H_2}} = 0.8811atm$$

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

[redacted]

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

The question asks for grams per liter, so:

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

Q.39

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

Solution

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

Q.41

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

Solution

At $20.0°\mathrm{C}$, water $\mathrm{H_2O}$ has a greater surface tension ($72.86\frac{mN}{m}$) than benzene, ($\mathrm{C_6H_6}$), ($28.88\frac{mN}{m}$) because the intermolecular forces between water molecules are stronger than the intermolecular forces between benzene

molecules. Water is capable of forming hydrogen-bonds, whereas the only forces that act in benzene are London dispersion forces.

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

Q.43

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

Solution

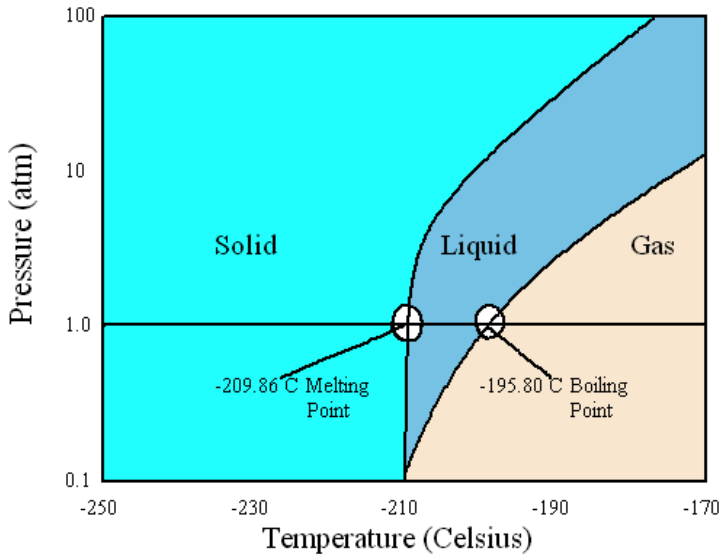
Compression favors the denser phase. Since Ga is a solid at $301.9K$, then it will undergo a phase change to become a liquid.

Q.45

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

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

Solution



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

Q.47

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

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

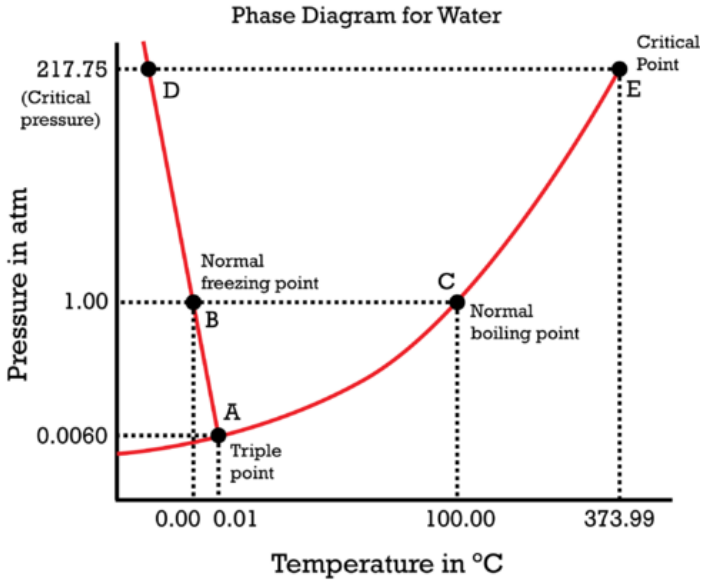


Figure used with permission (CK-12 Foundation – Christopher Auyeung)

Solution

Using the phase diagram of water,

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

Q.53

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

Solution

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

Q.59

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

Solution

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

$$PV = nRT$$

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

$$n = 162.77mols$$

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

Q.65

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

Relevant Information:

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

Solution

This question is a bit tricky. The coolants Liquid Nitrogen and Dry ice, ($CO_2\,(s)$), both turn into gasses at very low temperatures. After they turn into gaseous, they are no longer "useful", since they cannot be added into the bath. Therefore, after adding sufficient amounts of either of the coolants to either of the liquids, the temperature of the bath would decrease way past the freezing point of either liquid, resulting in a cooling "block" rather than a bath. So what is the deal? Is this problem unsolvable?

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

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

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

Q.71

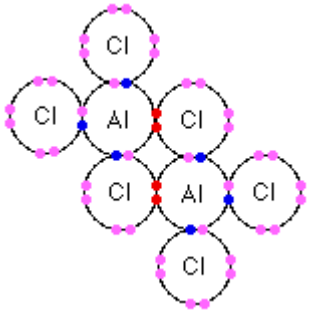
The melting points of the chlorides of third period elements are: $NaCl = 1074\ K$, $MgCl_2 = 987\ K$, $AlCl_3 = 465\ K$, $SiCl_4 = 204.4\ K$, $PCl_3 = 179\ K$. Based on the applicable intermolecular forces present in each compound, explain this trend in melting points.

Solution

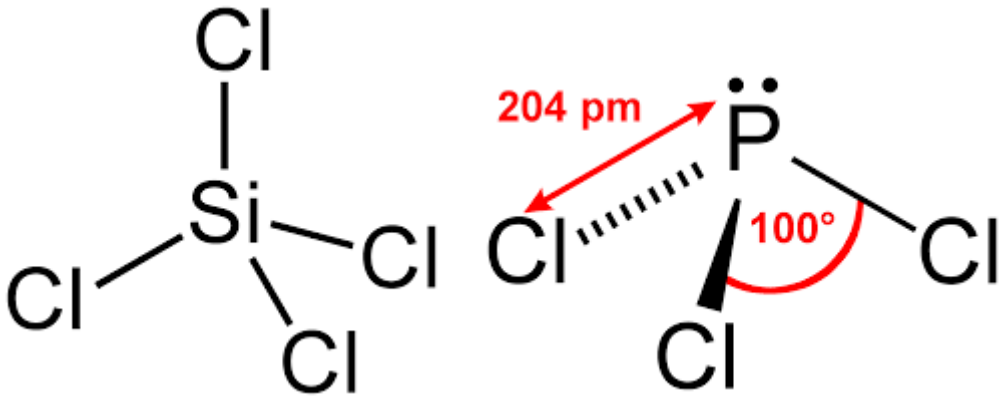
Experimentally, as the chloride compounds make their way across the third period elements, the melting points gradually decrease. This may appear an easy question to address since the melting points are a also measure of the magnitude of the intermolecular forces as play in the specific system, however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

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

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



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



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

Q.71

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

Solution

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

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

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4.0: Types of Solutions - Some Terminology

Learning Objectives

- To understand how enthalpy and entropy changes affect solution formation.
- To use the magnitude of the changes in both enthalpy and entropy to predict whether a given solute–solvent combination will spontaneously form a solution.

In all solutions, whether gaseous, liquid, or solid, the substance present in the greatest amount is the solvent, and the substance or substances present in lesser amounts are the solute(s). The solute does not have to be in the same physical state as the solvent, but the physical state of the solvent usually determines the state of the solution. As long as the solute and solvent combine to give a homogeneous solution, the solute is said to be soluble in the solvent. Table $4.0.1$ lists some common examples of gaseous, liquid, and solid solutions and identifies the physical states of the solute and solvent in each.

Table $4.0.1$: Types of Solutions

Solution	Solute	Solvent	Examples
gas	gas	gas	air, natural gas
liquid	gas	liquid	seltzer water (CO_2 gas in water)
liquid	liquid	liquid	alcoholic beverage (ethanol in water), gasoline
liquid	solid	liquid	tea, salt water
solid	gas	solid	H_2 in Pd (used for H_2 storage)
solid	solid	liquid	mercury in silver or gold (amalgam often used in dentistry)

The formation of a solution from a solute and a solvent is a physical process, not a chemical one. That is, both solute and solvent can be recovered in chemically unchanged forms using appropriate separation methods. For example, solid zinc nitrate dissolves in water to form an aqueous solution of zinc nitrate:

$$\mathrm{Zn(NO_3)_2\,(s) + H_2O\,(l)\ \rightarrow Zn^{2+}\,(aq) + 2\,NO_3^-\,(aq)}$$

Because $\mathrm{Zn(NO_3)_2}$ can be recovered easily by evaporating the water, this is a physical process. In contrast, metallic zinc appears to dissolve in aqueous hydrochloric acid. In fact, the two substances undergo a chemical reaction to form an aqueous solution of zinc chloride with evolution of hydrogen gas:

$$\mathrm{Zn\,(s) + 2\,H^+\,(aq) + 2\,Cl^-\,(aq)\ \rightarrow Zn^{2+}\,(aq) + 2\,Cl^-\,(aq) + H_2\,(g)}$$

> *Dissolution of a solute in a solvent to form a solution typically does not involve a chemical transformation and largely consist of breaking intermolecular forces rather than covalent bonds.*

When the solution evaporates, we do not recover metallic zinc, so we cannot say that metallic zinc is soluble in aqueous hydrochloric acid because it is chemically transformed when it dissolves. The dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.

Mercury Amalgams: Examples of solid Solutions

An amalgam is an alloy of mercury with another metal. It may be a liquid, a soft paste or a solid, depending upon the proportion of mercury. These alloys are formed through metallic bonding, with the electrostatic attractive force of the conduction electrons working to bind all the positively charged metal ions together into a crystal

lattice structure. Almost all metals can form amalgams with mercury including aluminum (Video 4.0.1), the notable exceptions being iron, platinum, tungsten, and tantalum. Silver-mercury amalgams are important in dentistry, and gold-mercury amalgam is used in the extraction of gold from ore.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

https://www.youtube.com/embed/IrdYueB9pY4?vq=hd1080

Video 4.0.1: Aluminum dissolving into Mercury.

Substances that form a single homogeneous phase in all proportions are said to be completely **miscible** in one another. Ethanol and water are miscible, just as mixtures of gases are miscible. If two substances are essentially insoluble in each other, such as oil and water, they are immiscible. Examples of gaseous solutions that we have already discussed include Earth's atmosphere.

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4.1: Composition of Solutions

Learning Objectives

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

There are several different ways to quantitatively describe the concentration of a solution. For example, molarity is a useful way to describe solution concentrations for reactions that are carried out in solution. Mole fractions are used not only to describe gas concentrations but also to determine the vapor pressures of mixtures of similar liquids. Example 4.1.1 reviews the methods for calculating the molarity and mole fraction of a solution when the masses of its components are known.

Example 4.1.1: Molarity and Mole Fraction

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

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

Given: mass of substance and mass and density of solution

Asked for: molarity and mole fraction

Strategy:

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

Solution:

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

$$\text{moles } CH_3CO_2H = \frac{3.78 \cancel{\text{ g}}\ CH_3CO_2H}{60.05 \cancel{\text{ g}}/\text{mol}}$$

$$= 0.0629 \text{ mol}$$

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

$$\text{volume} = \frac{\text{mass}}{\text{density}}$$

$$= \frac{100.0 \cancel{\text{ g}}\ \text{solution}}{1.00 \cancel{\text{ g}}/m\,\text{L}} = 100\ mL$$

Then calculate the molarity directly.

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

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

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

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

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

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

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

Exercise 4.1.1: Molarity and Mole Fraction

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

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

Answer a

6.10 M HCl

Answer b

$\chi_{HCl} = 0.111$

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

[redacted]

Molality, therefore, has the same numerator as molarity (the number of moles of solute) but a different denominator (kilogram of solvent rather than liter of solution). For dilute aqueous solutions, the molality and molarity are nearly the same because dilute solutions are mostly solvent. Thus because the density of water under standard conditions is very close to 1.0 g/mL, the volume of

1.0 kg of H_2O under these conditions is very close to 1.0 L, and a 0.50 M solution of KBr in water, for example, has approximately the same concentration as a 0.50 m solution.

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

In the health sciences, the concentration of a solution is often expressed as parts per thousand (ppt), indicated as a proportion. For example, adrenalin, the hormone produced in high-stress situations, is available in a 1:1000 solution, or one gram of adrenalin per 1000 g of solution.

The labels on bottles of commercial reagents often describe the contents in terms of mass percentage. Sulfuric acid, for example, is sold as a 95% aqueous solution, or 95 g of $\mathrm{H_2SO_4}$ per 100 g of solution. Parts per million and parts per billion are used to describe concentrations of highly dilute solutions. These measurements correspond to milligrams and micrograms of solute per kilogram of solution, respectively. For dilute aqueous solutions, this is equal to milligrams and micrograms of solute per liter of solution (assuming a density of 1.0 g/mL).

Example 4.1.2: Molarity and Mass

Several years ago, millions of bottles of mineral water were contaminated with benzene at ppm levels. This incident received a great deal of attention because the lethal concentration of benzene in rats is 3.8 ppm. A 250 mL sample of mineral water has 12.7 ppm of benzene. Because the contaminated mineral water is a very dilute aqueous solution, we can assume that its density is approximately 1.00 g/mL.

a. What is the molarity of the solution?
b. What is the mass of benzene in the sample?

Given: volume of sample, solute concentration, and density of solution

Asked for: molarity of solute and mass of solute in 250 mL

Strategy:

A. Use the concentration of the solute in parts per million to calculate the molarity.
B. Use the concentration of the solute in parts per million to calculate the mass of the solute in the specified volume of solution.

Solution:

a. A To calculate the molarity of benzene, we need to determine the number of moles of benzene in 1 L of solution. We know that the solution contains 12.7 ppm of benzene. Because 12.7 ppm is equivalent to 12.7 mg/1000 g of solution and the density of the solution is 1.00 g/mL, the solution contains 12.7 mg of benzene per liter (1000 mL). The molarity is therefore

$$\begin{aligned}\text{molarity} &= \frac{\text{moles}}{\text{liter solution}} \\ &= \frac{(12.7\ \cancel{mg})\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{1\ mol}{78.114\ \cancel{g}}\right)}{1.00\ L} \\ &= 1.63 \times 10^{-4} M\end{aligned}$$

b. B We are given that there are 12.7 mg of benzene per 1000 g of solution, which is equal to 12.7 mg/L of solution. Hence the mass of benzene in 250 mL (250 g) of solution is

$$\text{mass of benzene} = \frac{(12.7\ mg\ \text{benzene})(250\ \cancel{mL})}{1000\ \cancel{mL}}$$
$$= 3.18\ mg$$
$$= 3.18 \times 10^{-3}\ g\ \text{benzene}$$

Exercise 4.1.2: Molarity of Lead Solution

The maximum allowable concentration of lead in drinking water is 9.0 ppb.

a. What is the molarity of Pb^{2+} in a 9.0 ppb aqueous solution?
b. Use your calculated concentration to determine how many grams of Pb^{2+} are in an 8 oz glass of water.

Answer a

4.3×10^{-8} M

Answer b

2×10^{-6} g

How do chemists decide which units of concentration to use for a particular application? Although molarity is commonly used to express concentrations for reactions in solution or for titrations, it does have one drawback—molarity is the number of moles of solute divided by the volume of the solution, and the volume of a solution depends on its density, which is a function of temperature. Because volumetric glassware is calibrated at a particular temperature, typically 20°C, the molarity may differ from the original value by several percent if a solution is prepared or used at a significantly different temperature, such as 40°C or 0°C. For many applications this may not be a problem, but for precise work these errors can become important. In contrast, mole fraction, molality, and mass percentage depend on only the masses of the solute and solvent, which are independent of temperature.

Mole fraction is not very useful for experiments that involve quantitative reactions, but it is convenient for calculating the partial pressure of gases in mixtures, as discussed previously. Mole fractions are also useful for calculating the vapor pressures of certain types of solutions. Molality is particularly useful for determining how properties such as the freezing or boiling point of a solution vary with solute concentration. Because mass percentage and parts per million or billion are simply different ways of expressing the ratio of the mass of a solute to the mass of the solution, they enable us to express the concentration of a substance even when the molecular mass of the substance is unknown. Units of ppb or ppm are also used to express very low concentrations, such as those of residual impurities in foods or of pollutants in environmental studies.

Table 4.1.1 summarizes the different units of concentration and typical applications for each. When the molar mass of the solute and the density of the solution are known, it becomes relatively easy with practice to convert among the units of concentration we have discussed, as illustrated in Example 4.1.3.

*Table 4.1.1: Different Units for Expressing the Concentrations of Solutions**

Unit	Definition	Application
molarity (M)	moles of solute/liter of solution (mol/L)	Used for quantitative reactions in solution and titrations; mass and molecular mass of solute and volume of solution are known.
mole fraction (χ)	moles of solute/total moles present (mol/mol)	Used for partial pressures of gases and vapor pressures of some solutions; mass and molecular mass of each component are known.
molality (m)	moles of solute/kg of solvent (mol/kg)	Used in determining how colligative properties vary with solute concentration; masses and molecular mass of solute are known.

***The molarity of a solution is temperature dependent, but the other units shown in this table are independent of temperature.**

Unit	Definition	Application
mass percentage (%)	[mass of solute (g)/mass of solution (g)] × 100	Useful when masses are known but molecular masses are unknown.
parts per thousand (ppt)	[mass of solute/mass of solution] × 10^3 (g solute/kg solution)	Used in the health sciences, ratio solutions are typically expressed as a proportion, such as 1:1000.
parts per million (ppm)	[mass of solute/mass of solution] × 10^6 (mg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.
parts per billion (ppb)	[mass of solute/mass of solution] × 10^9 (µg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.
***The molarity of a solution is temperature dependent, but the other units shown in this table are independent of temperature.**		

Example 4.1.3: Vodka

Vodka is essentially a solution of ethanol in water. Typical vodka is sold as "80 proof," which means that it contains 40.0% ethanol by volume. The density of pure ethanol is 0.789 g/mL at 20°C. If we assume that the volume of the solution is the sum of the volumes of the components (which is not strictly correct), calculate the following for the ethanol in 80-proof vodka.

a. the mass percentage
b. the mole fraction
c. the molarity
d. the molality

Given: volume percent and density

Asked for: mass percentage, mole fraction, molarity, and molality

Strategy:

A. Use the density of the solute to calculate the mass of the solute in 100.0 mL of solution. Calculate the mass of water in 100.0 mL of solution.
B. Determine the mass percentage of solute by dividing the mass of ethanol by the mass of the solution and multiplying by 100.
C. Convert grams of solute and solvent to moles of solute and solvent. Calculate the mole fraction of solute by dividing the moles of solute by the total number of moles of substances present in solution.
D. Calculate the molarity of the solution: moles of solute per liter of solution. Determine the molality of the solution by dividing the number of moles of solute by the kilograms of solvent.

Solution:

The key to this problem is to use the density of pure ethanol to determine the mass of ethanol (CH_3CH_2OH), abbreviated as EtOH, in a given volume of solution. We can then calculate the number of moles of ethanol and the concentration of ethanol in any of the required units. A Because we are given a percentage by volume, we assume that we have 100.0 mL of solution. The volume of ethanol will thus be 40.0% of 100.0 mL, or 40.0 mL of ethanol, and the volume of water will be 60.0% of 100.0 mL, or 60.0 mL of water. The mass of ethanol is obtained from its density:

$$mass\ of\ EtOH = (40.0\ \cancel{mL}) \left(\frac{0.789\ g}{\cancel{mL}} \right) = 31.6\ g\ EtOH$$

If we assume the density of water is 1.00 g/mL, the mass of water is 60.0 g. We now have all the information we need to calculate the concentration of ethanol in the solution.

B The mass percentage of ethanol is the ratio of the mass of ethanol to the total mass of the solution, expressed as a percentage:

$$\begin{aligned} \%EtOH &= \left(\frac{mass\ of\ EtOH}{mass\ of\ solution} \right) (100) \\ &= \left(\frac{31.6\ \cancel{g}\ EtOH}{31.6\ \cancel{g}\ EtOH + 60.0\ \cancel{g}\ H_2O} \right) (100) \\ &= 34.5\% \end{aligned}$$

C The mole fraction of ethanol is the ratio of the number of moles of ethanol to the total number of moles of substances in the solution. Because 40.0 mL of ethanol has a mass of 31.6 g, we can use the molar mass of ethanol (46.07 g/mol) to determine the number of moles of ethanol in 40.0 mL:

$$\begin{aligned} moles\ CH_3CH_2OH &= (31.6\ \cancel{g\ CH_3CH_2OH}) \left(\frac{1\ mol}{46.07\ \cancel{g\ CH_3CH_2OH}} \right) \\ &= 0.686\ mol\ CH_3CH_2OH \end{aligned}$$

Similarly, the number of moles of water is

$$moles\ H_2O = (60.0\ \cancel{g\ H_2O}) \left(\frac{1\ mol\ H_2O}{18.02\ \cancel{g\ H_2O}} \right) = 3.33\ mol\ H_2O$$

The mole fraction of ethanol is thus

$$\chi_{CH_3CH_2OH} = \frac{0.686\ \cancel{mol}}{0.686\ \cancel{mol} + 3.33\ \cancel{mol}} = 0.171$$

D The molarity of the solution is the number of moles of ethanol per liter of solution. We already know the number of moles of ethanol per 100.0 mL of solution, so the molarity is

$$M_{CH_3CH_2OH} = \left(\frac{0.686\ mol}{100\ \cancel{mL}} \right) \left(\frac{1000\ \cancel{mL}}{L} \right) = 6.86\ M$$

The molality of the solution is the number of moles of ethanol per kilogram of solvent. Because we know the number of moles of ethanol in 60.0 g of water, the calculation is again straightforward:

$$m_{CH_3CH_2OH} = \left(\frac{0.686\ mol\ EtOH}{60.0\ \cancel{g}\ H_2O} \right) \left(\frac{1000\ \cancel{g}}{kg} \right) = \frac{11.4\ mol\ EtOH}{kg\ H_2O} = 11.4\ m$$

Exercise 4.1.3: Toluene/Benzene Solution

A solution is prepared by mixing 100.0 mL of toluene with 300.0 mL of benzene. The densities of toluene and benzene are 0.867 g/mL and 0.874 g/mL, respectively. Assume that the volume of the solution is the sum of the volumes of the components. Calculate the following for toluene.

a. mass percentage
b. mole fraction
c. molarity
d. molality

Answer a

mass percentage toluene = 24.8%

Answer b

$\chi_{toluene} = 0.219$

Answer c

2.35 M toluene

Answer d

3.59 m toluene

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Summary

Different units are used to express the concentrations of a solution depending on the application. The concentration of a solution is the quantity of solute in a given quantity of solution. It can be expressed in several ways: molarity (moles of solute per liter of solution); mole fraction, the ratio of the number of moles of solute to the total number of moles of substances present; mass percentage, the ratio of the mass of the solute to the mass of the solution times 100; parts per thousand (ppt), grams of solute per kilogram of solution; parts per million (ppm), milligrams of solute per kilogram of solution; parts per billion (ppb), micrograms of solute per kilogram of solution; and molality (m), the number of moles of solute per kilogram of solvent.

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IV: SOLUTIONS

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

4.0: Types of Solutions - Some Terminology

4.1: Composition of Solutions

4.2: Nature of Dissolved Species

4.3: Phase Equilibrium in Solutions - Nonvolatile Solutes

4.4: Phase Equilibrium in Solutions - Volatile Solutes

4.5: Separating Volatile Solutions - Distillation

4.6: Colloidal Suspensions

4.E: Solutions (Exercises)

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4.2: Nature of Dissolved Species

Learning Objectives

- To understand how enthalpy and entropy changes affect solution formation.
- To use the magnitude of the changes in both enthalpy and entropy to predict whether a given solute–solvent combination will spontaneously form a solution.

In all solutions, whether gaseous, liquid, or solid, the substance present in the greatest amount is the solvent, and the substance or substances present in lesser amounts are the solute(s). The solute does not have to be in the same physical state as the solvent, but the physical state of the solvent usually determines the state of the solution. As long as the solute and solvent combine to give a homogeneous solution, the solute is said to be soluble in the solvent. Table $4.2.1$ lists some common examples of gaseous, liquid, and solid solutions and identifies the physical states of the solute and solvent in each.

Table $4.2.1$: Types of Solutions

Solution	Solute	Solvent	Examples
gas	gas	gas	air, natural gas
liquid	gas	liquid	seltzer water (CO_2 gas in water)
liquid	liquid	liquid	alcoholic beverage (ethanol in water), gasoline
liquid	solid	liquid	tea, salt water
solid	gas	solid	H_2 in Pd (used for H_2 storage)
solid	solid	liquid	mercury in silver or gold (amalgam often used in dentistry)
solid	solid	solid	alloys and other "solid solutions"

Forming a Solution

The formation of a solution from a solute and a solvent is a physical process, not a chemical one. That is, both solute and solvent can be recovered in chemically unchanged forms using appropriate separation methods. For example, solid zinc nitrate dissolves in water to form an aqueous solution of zinc nitrate:



Because $Zn(NO_3)_2$ can be recovered easily by evaporating the water, this is a physical process. In contrast, metallic zinc appears to dissolve in aqueous hydrochloric acid. In fact, the two substances undergo a chemical reaction to form an aqueous solution of zinc chloride with evolution of hydrogen gas:



When the solution evaporates, we do not recover metallic zinc, so we cannot say that metallic zinc is soluble in aqueous hydrochloric acid because it is chemically transformed when it dissolves. The dissolution of a solute in a solvent to form a solution does not involve a chemical transformation (that it is a physical change).

> Dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.

Substances that form a single homogeneous phase in all proportions are said to be completely *miscible* in one another. Ethanol and water are miscible, just as mixtures of gases are miscible. If two substances are essentially insoluble in each other, such as oil and water, they are *immiscible*. Examples of gaseous solutions that we have already discussed include Earth's atmosphere.

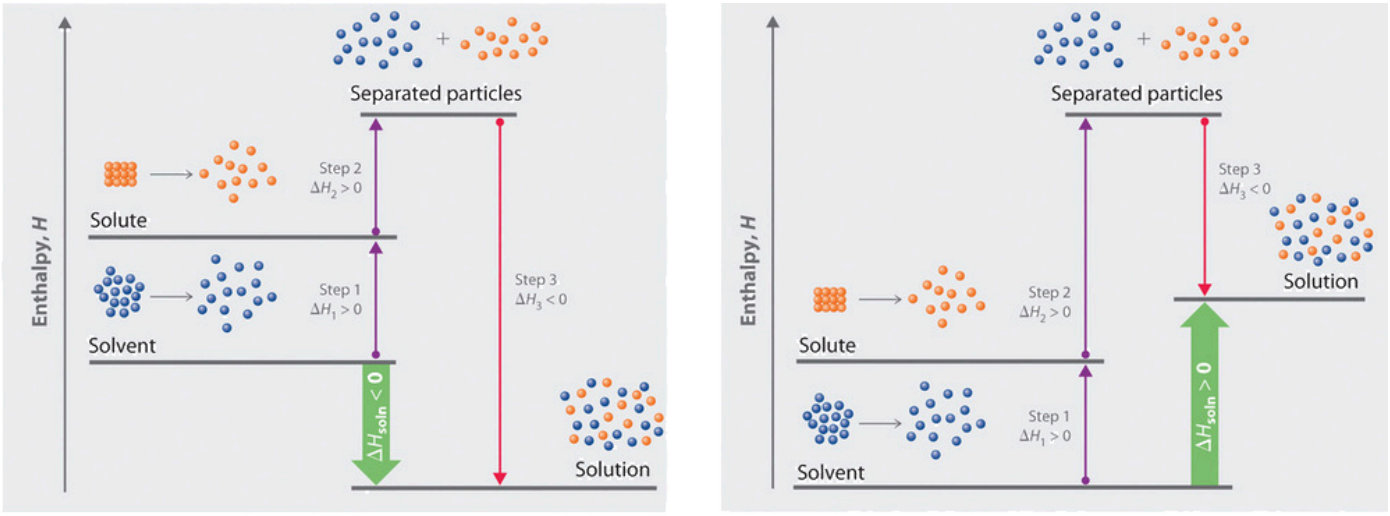
The Role of Enthalpy in Solution Formation

Energy is required to overcome the intermolecular interactions in a solute, which can be supplied only by the new interactions that occur in the solution, when each solute particle is surrounded by particles of the solvent in a process called solvation (or hydration when the solvent is water). Thus all of the solute–solute interactions and many of the solvent–solvent interactions must be disrupted for a solution to form. In this section, we describe the role of enthalpy in this process.

Because enthalpy is a state function, we can use a thermochemical cycle to analyze the energetics of solution formation. The process occurs in three discrete steps, indicated by ΔH_1, ΔH_2, and ΔH_3 in Figure 4.2.2. The overall enthalpy change in the formation of the solution (ΔH_{soln}) is the sum of the enthalpy changes in the three steps:

[redacted]

When a solvent is added to a solution, steps 1 and 2 are both endothermic because energy is required to overcome the intermolecular interactions in the solvent (ΔH_1) and the solute (ΔH_2). Because ΔH is positive for both steps 1 and 2, the solute–solvent interactions (ΔH_3) must be stronger than the solute–solute and solvent–solvent interactions they replace in order for the dissolution process to be exothermic ($\Delta H_{soln} < 0$). When the solute is an ionic solid, ΔH_2 corresponds to the lattice energy that must be overcome to form a solution. The higher the charge of the ions in an ionic solid, the higher the lattice energy. Consequently, solids that have very high lattice energies, such as MgO (–3791 kJ/mol), are generally insoluble in all solvents.



(a) Exothermic solution formation **(b) Endothermic solution formation**

Figure 4.2.2: Enthalpy Changes That Accompany the Formation of a Solution. Solvation can be an exothermic or endothermic process depending on the nature of the solute and solvent. In both cases, step 1, separation of the solvent particles, is energetically uphill ($\Delta H_1 > 0$), as is step 2, separation of the solute particles ($\Delta H_2 > 0$). In contrast, energy is released in step 3 ($\Delta H_3 < 0$) because of interactions between the solute and solvent. (a) When ΔH_3 is larger in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is exothermic ($\Delta H_{soln} < 0$), as shown in the thermochemical cycle. (b) When ΔH_3 is smaller in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is endothermic ($\Delta H_{soln} > 0$).

A positive value for ΔH_{soln} does not mean that a solution will not form. Whether a given process, including formation of a solution, occurs spontaneously depends on whether the total energy of the system is lowered as a result. Enthalpy is only one of the contributing factors. A high ΔH_{soln} is usually an indication that the substance is not very soluble. Instant cold packs used to treat athletic injuries, for example, take advantage of the large positive ΔH_{soln} of ammonium nitrate during dissolution (+25.7 kJ/mol), which produces temperatures less than 0°C (Figure 4.2.3).



Figure 4.2.3: Commercial Cold Packs for Treating Injuries. These packs contain solid NH_4NO_3 and water in separate compartments. When the seal between the compartments is broken, the NH_4NO_3 dissolves in the water. Because ΔH_{soln} for NH_4NO_3 is much greater than zero, heat is absorbed by the cold pack during the dissolution process, producing local temperatures less than 0°C.

Entropy and Solution Formation

The enthalpy change that accompanies a process is important because processes that release substantial amounts of energy tend to occur spontaneously. A second property of any system, its entropy, is also important in helping us determine whether a given process occurs spontaneously. We will discuss entropy in more detail elsewhere, but for now we can state that entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. A perfect crystal at 0 K, whose atoms are regularly arranged in a perfect lattice and are motionless, has an entropy of zero. In contrast, gases have large positive entropies because their molecules are highly disordered and in constant motion at high speeds.

The formation of a solution disperses molecules, atoms, or ions of one kind throughout a second substance, which generally increases the disorder and results in an increase in the entropy of the system. Thus entropic factors almost always favor formation of a solution. In contrast, a change in enthalpy may or may not favor solution formation. The London dispersion forces that hold cyclohexane and n-hexane together in pure liquids, for example, are similar in nature and strength. Consequently, ΔH_{soln} should be approximately zero, as is observed experimentally. Mixing equal amounts of the two liquids, however, produces a solution in which the n-hexane and cyclohexane molecules are uniformly distributed over approximately twice the initial volume. In this case, the driving force for solution formation is not a negative ΔH_{soln} but rather the increase in entropy due to the increased disorder in the mixture. All spontaneous processes with $\Delta H \geq 0$ are characterized by an *increase* in entropy. In other cases, such as mixing oil with water, salt with gasoline, or sugar with hexane, the enthalpy of solution is large and positive, and the increase in entropy resulting from solution formation is not enough to overcome it. Thus in these cases a solution does not form.

> All spontaneous processes with $\Delta H \geq 0$ are characterized by an increase in entropy.

Table 4.2.2 summarizes how enthalpic factors affect solution formation for four general cases. The column on the far right uses the relative magnitudes of the enthalpic contributions to predict whether a solution will form from each of the four. Keep in mind that in each case entropy favors solution formation. In two of the cases the enthalpy of solution is expected to be relatively small and can be either positive or negative. Thus the entropic contribution dominates, and we expect a solution to form readily. In the other two cases the enthalpy of solution is expected to be large and positive. The entropic contribution, though favorable, is usually too small to overcome the unfavorable enthalpy term. Hence we expect that a solution will not form readily.

*Table 4.2.2: Relative Changes in Enthalpies for Different Solute–Solvent Combinations**

ΔH_1 (separation of solvent molecules)	ΔH_2 (separation of solute particles)	ΔH_3 (solute–solvent interactions)	ΔH_{soln} (ΔH_1 + ΔH_2 +ΔH_3)	Result of Mixing Solute and Solvent†
large; positive	large; positive	large; negative	small; positive or negative	solution will usually form
small; positive	large; positive	small; negative	large; positive	solution will not form
large; positive	small; positive	small; negative	large; positive	solution will not form
small; positive	small; positive	small; negative	small; positive or negative	solution will usually form

*ΔH_1, ΔH_2, and ΔH_3 refer to the processes indicated in the thermochemical cycle shown in Figure 4.2.2.
†In all four cases, entropy increases.

In contrast to liquid solutions, the intermolecular interactions in gases are weak (they are considered to be nonexistent in ideal gases). Hence mixing gases is usually a thermally neutral process ($\Delta H_{soln} \approx 0$), and the entropic factor due to the increase in disorder is dominant (Figure 4.2.4). Consequently, all gases dissolve readily in one another in all proportions to form solutions.

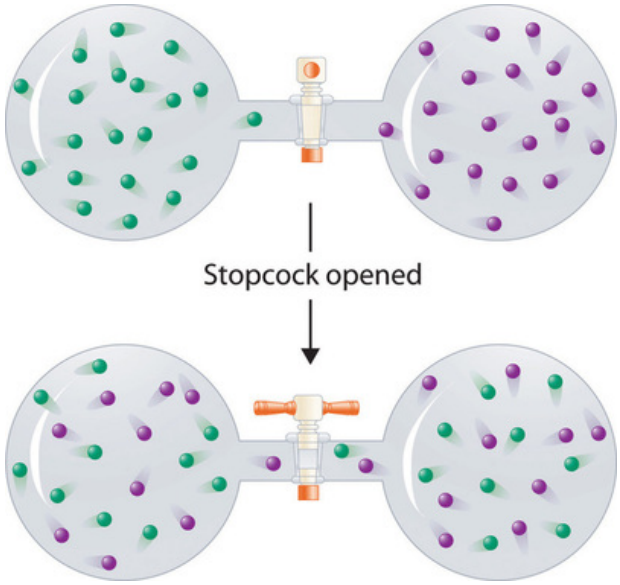
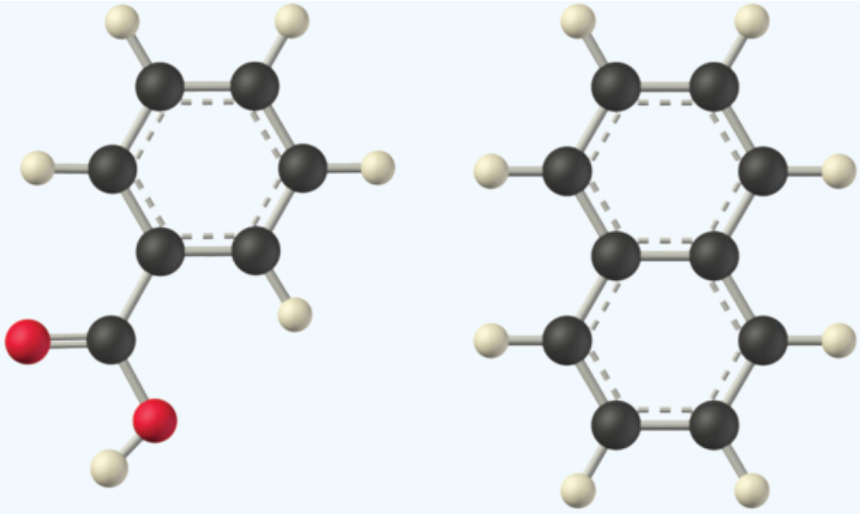


Figure 4.2.4: Formation of a Solution of Two Gases. (top) Pure samples of two different gases are in separate bulbs. (bottom) When the connecting stopcock is opened, diffusion causes the two gases to mix together and form a solution. Even though ΔH_{soln} is zero for the process, the increased entropy of the solution (the increased disorder) versus that of the separate gases favors solution formation.

Example 4.2.1

Considering LiCl, benzoic acid ($\mathrm{C_6H_5CO_2H}$), and naphthalene, which will be most soluble and which will be least soluble in water?



Benzoic acid Naphthalene

Given: three compounds

Asked for: relative solubilities in water

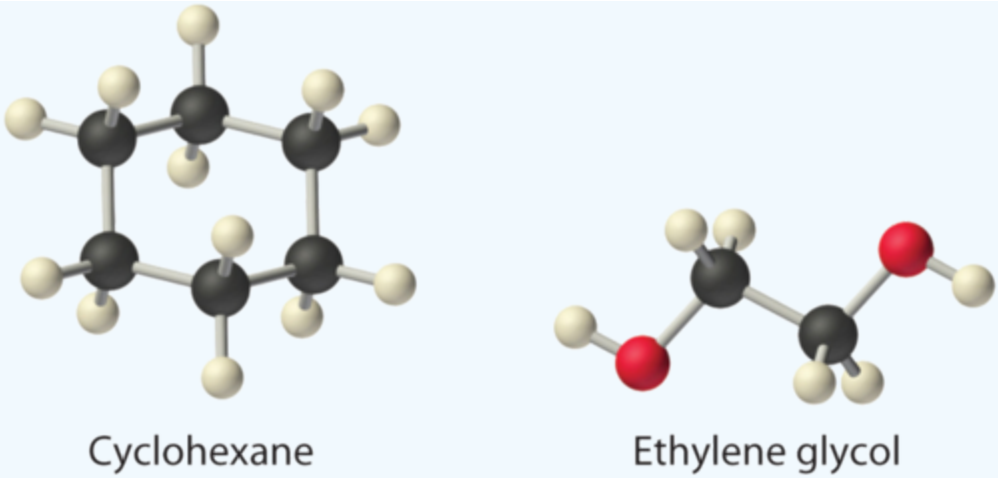
Strategy: Assess the relative magnitude of the enthalpy change for each step in the process shown in Figure 4.2.2 . Then use Table 4.2.2 to predict the solubility of each compound in water and arrange them in order of decreasing solubility.

Solution:

The first substance, LiCl, is an ionic compound, so a great deal of energy is required to separate its anions and cations and overcome the lattice energy (ΔH_2 is far greater than zero in Equation 4.2.1074). Because water is a polar substance, the interactions between both Li^+ and Cl^- ions and water should be favorable and strong. Thus we expect ΔH_3 to be far less than zero, making LiCl soluble in water. In contrast, naphthalene is a nonpolar compound, with only London dispersion forces holding the molecules together in the solid state. We therefore expect ΔH_2 to be small and positive. We also expect the interaction between polar water molecules and nonpolar naphthalene molecules to be weak $\Delta H_3 \approx 0$. Hence we do not expect naphthalene to be very soluble in water, if at all. Benzoic acid has a polar carboxylic acid group and a nonpolar aromatic ring. We therefore expect that the energy required to separate solute molecules (ΔH_2) will be greater than for naphthalene and less than for LiCl. The strength of the interaction of benzoic acid with water should also be intermediate between those of LiCl and naphthalene. Hence benzoic acid is expected to be more soluble in water than naphthalene but less soluble than LiCl. We thus predict LiCl to be the most soluble in water and naphthalene to be the least soluble.

Exercise 4.2.1

Considering ammonium chloride, cyclohexane, and ethylene glycol ($HOCH_2CH_2OH$), which will be most soluble and which will be least soluble in benzene?



Answer

The most soluble is cyclohexane; the least soluble is ammonium chloride.

Summary

Solutions are homogeneous mixtures of two or more substances whose components are uniformly distributed on a microscopic scale. The component present in the greatest amount is the solvent, and the components present in lesser amounts are the solute(s). The formation of a solution from a solute and a solvent is a physical process, not a chemical one. Substances that are miscible, such as gases, form a single phase in all proportions when mixed. Substances that form separate phases are immiscible. Solvation is the process in which solute particles are surrounded by solvent molecules. When the solvent is water, the process is called hydration. The overall enthalpy change that accompanies the formation of a solution, ΔH_{soln}, is the sum of the enthalpy change for breaking the intermolecular interactions in both the solvent and the solute and the enthalpy change for the formation of new solute–solvent interactions. Exothermic ($\Delta H_{soln} < 0$) processes favor solution formation. In addition, the change in entropy, the degree of disorder of the system, must be considered when predicting whether a solution will form. An increase in entropy (a decrease in order) favors dissolution.

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4.3: Phase Equilibrium in Solutions - Nonvolatile Solutes

Learning Objectives

- To describe the relationship between solute concentration and the physical properties of a solution.
- To understand that the total number of nonvolatile solute particles determines the decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus the pure solvent.

Many of the physical properties of solutions differ significantly from those of the pure substances discussed in earlier chapters, and these differences have important consequences. For example, the limited temperature range of liquid water (0°C–100°C) severely limits its use. Aqueous solutions have both a lower freezing point and a higher boiling point than pure water. Probably one of the most familiar applications of this phenomenon is the addition of ethylene glycol ("antifreeze") to the water in an automobile radiator. This solute lowers the freezing point of the water, preventing the engine from cracking in very cold weather from the expansion of pure water on freezing. Antifreeze also enables the cooling system to operate at temperatures greater than 100°C without generating enough pressure to explode.

Changes in the freezing point and boiling point of a solution depend primarily on the number of solute particles present rather than the kind of particles. Such properties of solutions are called colligative properties (from the Latin *colligatus*, meaning "bound together" as in a quantity). As we will see, the vapor pressure and osmotic pressure of solutions are also colligative properties.

Counting Concentrations and Effective Concentrations

When we determine the number of particles in a solution, it is important to remember that not all solutions with the same molarity contain the same concentration of solute particles. Consider, for example, 0.01 M aqueous solutions of sucrose, NaCl, and $\mathrm{CaCl_2}$. Because sucrose dissolves to give a solution of neutral molecules, the concentration of solute particles in a 0.01 M sucrose solution is 0.01 M. In contrast, both NaCl and $\mathrm{CaCl_2}$ are ionic compounds that dissociate in water to yield solvated ions. As a result, a 0.01 M aqueous solution of NaCl contains 0.01 M $\mathrm{Na^+}$ ions and 0.01 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.02 M. Similarly, the $\mathrm{CaCl_2}$ solution contains 0.01 M $\mathrm{Ca^{2+}}$ ions and 0.02 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.03 M. These values are correct for dilute solutions, where the dissociation of the compounds to form separately solvated ions is complete.

At **higher concentrations** (typically >1 M), especially with salts of small, highly charged ions (such as $\mathrm{Mg^{2+}}$ or $\mathrm{Al^{3+}}$), or in solutions with less polar solvents, dissociation to give separate ions is often incomplete. The sum of the concentrations of the dissolved solute particles dictates the physical properties of a solution. In the following discussion, we must therefore keep the chemical nature of the solute firmly in mind. A greater discussion of this is below.

Vapor Pressure of Solutions and Raoult's Law For Nonvolatile Solutes

Adding a nonvolatile solute, one whose vapor pressure is too low to measure readily, to a volatile solvent decreases the vapor pressure of the solvent. We can understand this phenomenon qualitatively by examining Figure $4.3.1$, which is a schematic diagram of the surface of a solution of glucose in water. In an aqueous solution of glucose, a portion of the surface area is occupied by nonvolatile glucose molecules rather than by volatile water molecules. As a result, fewer water molecules can enter the vapor phase per unit time, even though the surface water molecules have the same kinetic energy distribution as they would in pure water. At the same time, the rate at which water molecules in the vapor phase collide with the surface and reenter the solution is unaffected. The net effect is to shift the dynamic equilibrium between water in the vapor and the liquid phases, decreasing the vapor pressure of the solution compared with the vapor pressure of the pure solvent.

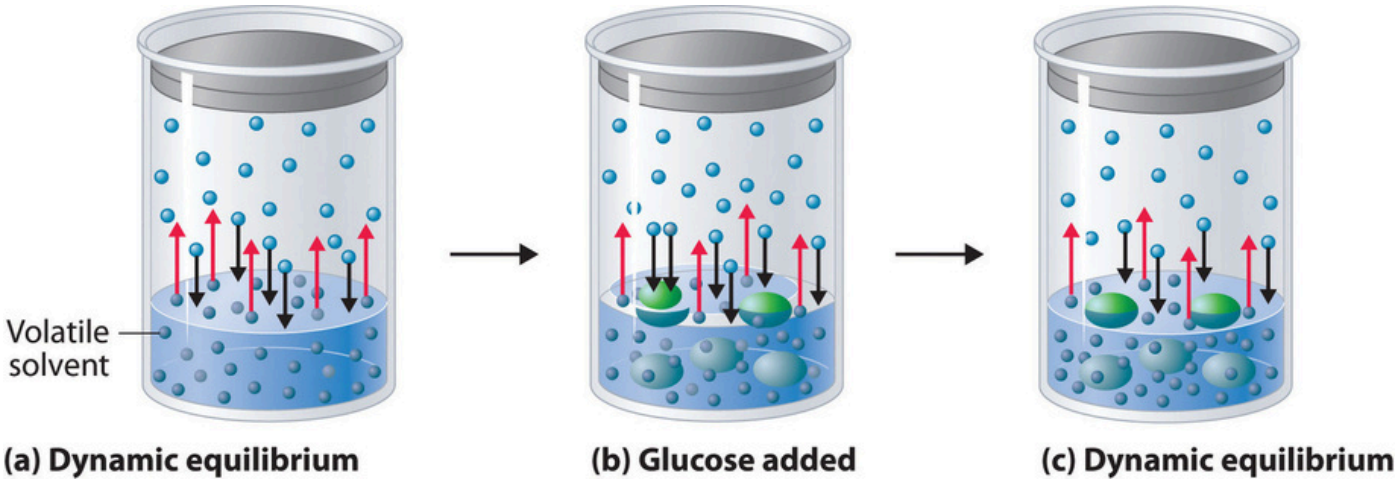


Figure 4.3.1: A Model Depicting Why the Vapor Pressure of a Solution of Glucose Is Less Than the Vapor Pressure of Pure Water. (a) When water or any volatile solvent is in a closed container, water molecules move into and out of the liquid phase at the same rate in a dynamic equilibrium. (b) If a nonvolatile solute such as glucose is added, some fraction of the surface area is occupied by solvated solute molecules. As a result, the rate at which water molecules evaporate is decreased, although initially their rate of condensation is unchanged. (c) When the glucose solution reaches equilibrium, the concentration of water molecules in the vapor phase, and hence the vapor pressure, is less than that of pure water. (CC BY-NC-SA; anonymous)

Figure 4.3.2 shows two beakers, one containing pure water and one containing an aqueous glucose solution, in a sealed chamber. We can view the system as having two competing equilibria: water vapor will condense in both beakers at the same rate, but water molecules will evaporate more slowly from the glucose solution because fewer water molecules are at the surface. Eventually all of the water will evaporate from the beaker containing the liquid with the higher vapor pressure (pure water) and condense in the beaker containing the liquid with the lower vapor pressure (the glucose solution). If the system consisted of only a beaker of water inside a sealed container, equilibrium between the liquid and vapor would be achieved rather rapidly, and the amount of liquid water in the beaker would remain constant.

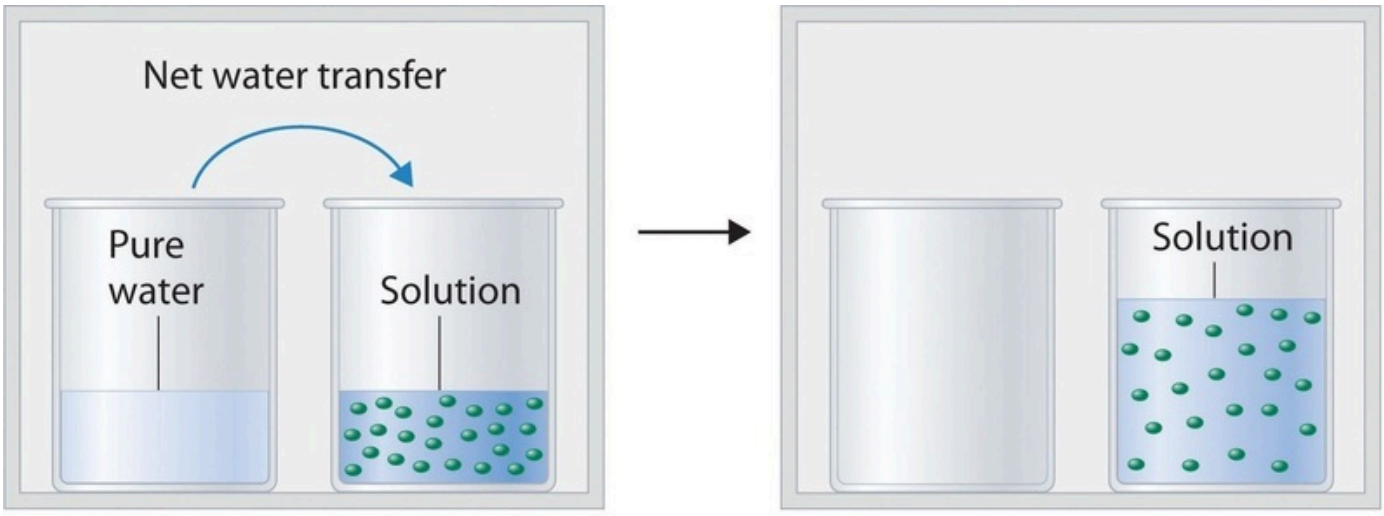


Figure 4.3.2: Transfer of Water to a Beaker Containing a Glucose Solution. (top) One beaker contains an aqueous solution of glucose, and the other contains pure water. If they are placed in a sealed chamber, the lower vapor pressure of water in the glucose solution results in a net transfer of water from the beaker containing pure water to the beaker containing the glucose solution. (bottom) Eventually, all of the water is transferred to the beaker that has the glucose solution. (CC BY-NC-SA; anonymous)

If the particles of a solute are essentially the same size as those of the solvent and both solute and solvent have roughly equal probabilities of being at the surface of the solution, then the effect of a solute on the vapor pressure of the solvent is proportional to the number of sites occupied by solute particles at the surface of the solution. Doubling the concentration of a given solute causes twice as many surface sites to be occupied by solute molecules, resulting in twice the decrease in vapor pressure. The relationship between solution composition and vapor pressure is therefore

where P_A is the vapor pressure of component A of the solution (in this case the solvent), χ_A is the mole fraction of A in solution, and P_A^0 is the vapor pressure of pure A. Equation 4.3.1077 is known as **Raoult's law**, after the French chemist who developed it. If the solution contains only a single nonvolatile solute (B), then we can relate the mole fraction of the solvent to the solute

$$\chi_A + \chi_B = 1$$

and we can substitute $\chi_A = 1 - \chi_B$ into Equation 4.3.1077 to obtain

$$\begin{aligned} P_A &= (1 - \chi_B)P_A^0 \\ &= P_A^0 - \chi_B P_A^0 \end{aligned}$$

Rearranging and defining $\Delta P_A = P_A^0 - P_A$, we obtain a relationship between the decrease in vapor pressure and the mole fraction of nonvolatile solute:

[redacted]

We can solve vapor pressure problems in either of two ways: by using Equation 4.3.1077 to calculate the actual vapor pressure above a solution of a nonvolatile solute, or by using Equation 4.3.1079 to calculate the decrease in vapor pressure caused by a specified amount of a nonvolatile solute.

Example 4.3.1: Anti-Freeze

Ethylene glycol ($HOCH_2CH_2OH$), the major ingredient in commercial automotive antifreeze, increases the boiling point of radiator fluid by lowering its vapor pressure. At 100°C, the vapor pressure of pure water is 760 mmHg. Calculate the vapor pressure of an aqueous solution containing 30.2% ethylene glycol by mass, a concentration commonly used in climates that do not get extremely cold in winter.

Given: identity of solute, percentage by mass, and vapor pressure of pure solvent

Asked for: vapor pressure of solution

Strategy:

A. Calculate the number of moles of ethylene glycol in an arbitrary quantity of water, and then calculate the mole fraction of water.
B. Use Raoult's law (Equation 4.3.1077) to calculate the vapor pressure of the solution.

Solution:

A A 30.2% solution of ethylene glycol contains 302 g of ethylene glycol per kilogram of solution; the remainder (698 g) is water. To use Raoult's law to calculate the vapor pressure of the solution, we must know the mole fraction of water. Thus we must first calculate the number of moles of both ethylene glycol (EG) and water present:

$$moles\ EG = (302\ \cancel{g}) \left(\frac{1\ mol}{62.07\ \cancel{g}} \right) = 4.87\ mol\ EG$$

$$moles\ H_2O = (698\ \cancel{g}) \left(\frac{1\ mol}{18.02\ \cancel{g}} \right) = 38.7\ mol\ H_2O$$

The mole fraction of water is thus

$$\chi_{H_2O} = \frac{38.7\ \cancel{mol}\ H_2O}{38.7\ \cancel{mol}\ H_2O + 4.87\ \cancel{mol}\ EG} = 0.888$$

B From Raoult's law (Equation 4.3.1077), the vapor pressure of the solution is

$$\begin{aligned} P_{\mathrm{H_2O}} &= (\chi_{\mathrm{H_2O}})(P^0_{\mathrm{H_2O}}) \\ &= (0.888)(760\ mmHg) = 675\ mmHg \end{aligned}$$

Alternatively, we could solve this problem by calculating the mole fraction of ethylene glycol and then using Equation 4.3.1079 to calculate the resulting decrease in vapor pressure:

$$\begin{aligned} \chi_{EG} &= \frac{4.87\ mol\ EG}{4.87\ mol\ EG + 38.7\ mol\ H_2O} \\ &= 0.112 \end{aligned}$$

$$\begin{aligned} \Delta P_{\mathrm{H_2O}} &= (\chi_{EG})(P^0_{\mathrm{H_2O}}) \\ &= (0.112)(760\ mmHg) = 85.1\ mmHg \end{aligned}$$

$$P_{\mathrm{H_2O}} = P^0_{\mathrm{H_2O}} - \Delta P_{\mathrm{H_2O}} = 760\ mmHg - 85.1\ mmHg = 675\ mmHg$$

The same result is obtained using either method.

Exercise 4.3.1

Seawater is an approximately 3.0% aqueous solution of NaCl by mass with about 0.5% of other salts by mass. Calculate the decrease in the vapor pressure of water at 25°C caused by this concentration of NaCl, remembering that 1 mol of NaCl produces 2 mol of solute particles. The vapor pressure of pure water at 25°C is 23.8 mmHg.

Answer

0.45 mmHg. This may seem like a small amount, but it constitutes about a 2% decrease in the vapor pressure of water and accounts in part for the higher humidity in the north-central United States near the Great Lakes, which are freshwater lakes. The decrease therefore has important implications for climate modeling.

Boiling Point Elevation

Recall that the normal boiling point of a substance is the temperature at which the vapor pressure equals 1 atm. If a nonvolatile solute lowers the vapor pressure of a solvent, it must also affect the boiling point. Because the vapor pressure of the solution at a given temperature is less than the vapor pressure of the pure solvent, achieving a vapor pressure of 1 atm for the solution requires a higher temperature than the normal boiling point of the solvent. Thus the boiling point of a solution is always greater than that of the pure solvent. We can see why this must be true by comparing the phase diagram for an aqueous solution with the phase diagram for pure water (Figure 4.3.4). The vapor pressure of the solution is less than that of pure water at all temperatures. Consequently, the liquid–vapor curve for the solution crosses the horizontal line corresponding to $P = 1\ atm$ at a higher temperature than does the curve for pure water.

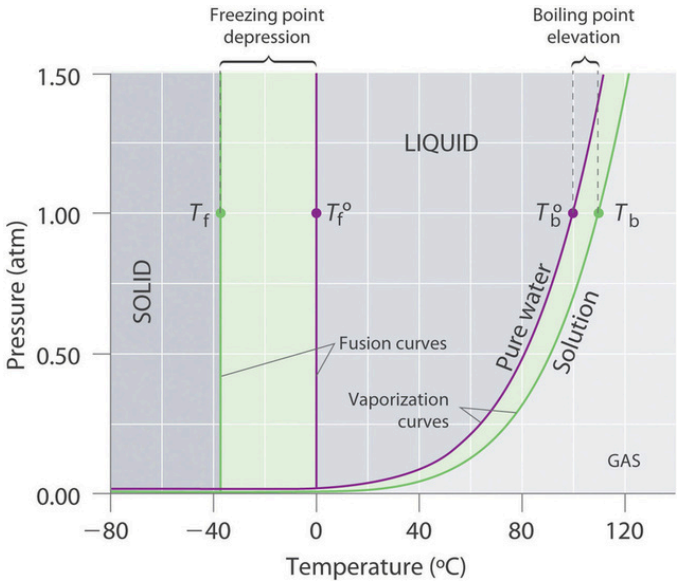


Figure 4.3.4: Phase Diagrams of Pure Water and an Aqueous Solution of a Nonvolatile Solute. The vaporization curve for the solution lies below the curve for pure water at all temperatures, which results in an increase in the boiling point and a decrease in the freezing point of the solution. (CC BY-NC-SA; anonymous)

The boiling point of a solution with a nonvolatile solute is **always** greater than the boiling point of the pure solvent.

The magnitude of the increase in the boiling point is related to the magnitude of the decrease in the vapor pressure. As we have just discussed, the decrease in the vapor pressure is proportional to the concentration of the solute in the solution. Hence the magnitude of the increase in the boiling point must also be proportional to the concentration of the solute (Figure 4.3.5).

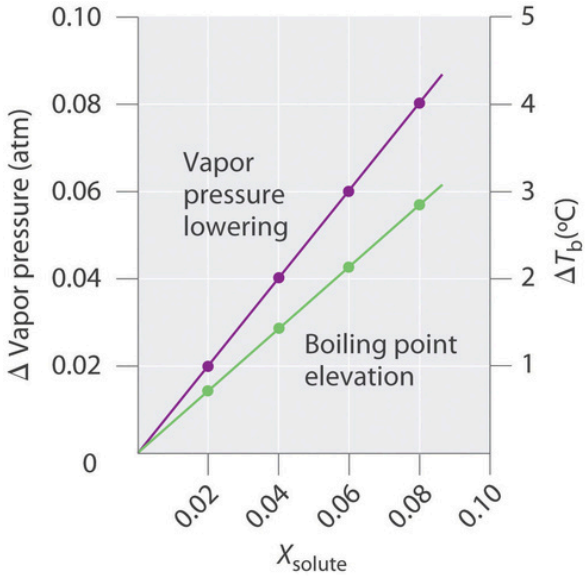


Figure 4.3.5: Vapor Pressure Decrease and Boiling Point Increase as Functions of the Mole Fraction of a Nonvolatile Solute. (CC BY-NC-SA; anonymous)

We can define the boiling point elevation (ΔT_b) as the difference between the boiling points of the solution and the pure solvent:

[redacted]

where T_b is the boiling point of the solution and T_b^0 is the boiling point of the pure solvent. We can express the relationship between ΔT_b and concentration as follows

[redacted]

where m is the concentration of the solute expressed in molality, and K_b is the **molal boiling point elevation constant** of the solvent, which has units of °C/m. Table 4.3.1 lists characteristic K_b values for several commonly used solvents. For relatively dilute solutions, the magnitude of both properties is proportional to the solute concentration.

Table 4.3.1: Boiling Point Elevation Constants (K_b) and Freezing Point Depression Constants (K_f) for Some Solvents

Solvent	Boiling Point (°C)	K_b (°C/m)	Freezing Point (°C)	K_f (°C/m)
acetic acid	117.90	3.22	16.64	3.63
benzene	80.09	2.64	5.49	5.07
d-(+)-camphor	207.4	4.91	178.8	37.8
carbon disulfide	46.2	2.42	−112.1	3.74
carbon tetrachloride	76.8	5.26	−22.62	31.4
chloroform	61.17	3.80	−63.41	4.60
nitrobenzene	210.8	5.24	5.70	6.87
water	100.00	0.51	0.00	1.86

The concentration of the solute is typically expressed as molality rather than mole fraction or molarity for two reasons. First, because the density of a solution changes with temperature, the value of molarity also varies with temperature. If the boiling point depends on the solute concentration, then by definition the system is not maintained at a constant temperature. Second, molality and mole fraction are proportional for relatively dilute solutions, but molality has a larger numerical value (a mole fraction can be only between zero and one). Using molality allows us to eliminate nonsignificant zeros.

According to Table 4.3.1, the molal boiling point elevation constant for water is 0.51°C/m. Thus a 1.00 m aqueous solution of a nonvolatile molecular solute such as glucose or sucrose will have an increase in boiling point of 0.51°C, to give a boiling point of 100.51°C at 1.00 atm. The increase in the boiling point of a 1.00 m aqueous NaCl solution will be approximately twice as large as that of the glucose or sucrose solution because 1 mol of NaCl produces 2 mol of dissolved ions. Hence a 1.00 m NaCl solution will have a boiling point of about 101.02°C.

Example 4.3.3

In Example 4.3.1, we calculated that the vapor pressure of a 30.2% aqueous solution of ethylene glycol at 100°C is 85.1 mmHg less than the vapor pressure of pure water. We stated (without offering proof) that this should result in a higher boiling point for the solution compared with pure water. Now that we have seen why this assertion is correct, calculate the boiling point of the aqueous ethylene glycol solution.

Given: composition of solution

Asked for: boiling point

Strategy:

Calculate the molality of ethylene glycol in the 30.2% solution. Then use Equation 4.3.1081 to calculate the increase in boiling point.

Solution:

From Example 4.3.1, we know that a 30.2% solution of ethylene glycol in water contains 302 g of ethylene glycol (4.87 mol) per 698 g of water. The molality of the solution is thus

$$\text{molality of ethylene glycol} = \left(\frac{4.87\ mol}{698\ \cancel{g}\ H_2O}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right)$$
$$= 6.98\,m$$

From Equation 4.3.1081, the increase in boiling point is therefore

$$\begin{aligned}\Delta T_b &= mK_b \\ &= (6.98\,\cancel{m})(0.51°C/\cancel{m}) \\ &= 3.6°C\end{aligned}$$

The boiling point of the solution is thus predicted to be 104°C. With a solute concentration of almost 7 m, however, the assumption of a dilute solution used to obtain Equation 4.3.1081 may not be valid.

Exercise 4.3.3

Assume that a tablespoon (5.00 g) of NaCl is added to 2.00 L of water at 20.0°C, which is then brought to a boil to cook spaghetti. At what temperature will the water boil?

Answer

100.04°C, or 100°C to three significant figures. (Recall that 1 mol of NaCl produces 2 mol of dissolved particles. The small increase in temperature means that adding salt to the water used to cook pasta has essentially no effect on the cooking time.)

Freezing Point Depression

The phase diagram in Figure 4.3.4 shows that dissolving a nonvolatile solute in water not only raises the boiling point of the water but also lowers its freezing point. The solid–liquid curve for the solution crosses the line corresponding to $P = 1\ atm$ at a lower temperature than the curve for pure water.

We can understand this result by imagining that we have a sample of water at the normal freezing point temperature, where there is a dynamic equilibrium between solid and liquid. Water molecules are continuously colliding with the ice surface and entering the solid phase at the same rate that water molecules are leaving the surface of the ice and entering the liquid phase. If we dissolve a nonvolatile solute such as glucose in the liquid, the dissolved glucose molecules will reduce the number of collisions per unit time between water molecules and the ice surface because some of the molecules colliding with the ice will be glucose. Glucose, though, has a very different structure than water, and it cannot fit into the ice lattice. Consequently, the presence of glucose molecules in the solution can only decrease the rate at which water molecules in the liquid collide with the ice surface and solidify. Meanwhile, the rate at which the water molecules leave the surface of the ice and enter the liquid phase is unchanged. The net effect is to cause the ice to melt. The only way to reestablish a dynamic equilibrium between solid and liquid water is to lower the temperature of the system, which decreases the rate at which water molecules leave the surface of the ice crystals until it equals the rate at which water molecules in the solution collide with the ice.

By analogy to our treatment of boiling point elevation,the freezing point depression (ΔT_f) is defined as the difference between the freezing point of the pure solvent and the freezing point of the solution:

[redacted]

where T_f^0 is the freezing point of the pure solvent and T_f is the freezing point of the solution.

The order of the terms is reversed compared with Equation 4.3.1080 to express the freezing point depression as a positive number. The relationship between ΔT_f and the solute concentration is given by an equation analogous to Equation 4.3.1081:

[redacted]

where m is the molality of the solution and K_f is the molal freezing point depression constant for the solvent (in units of °C/m).

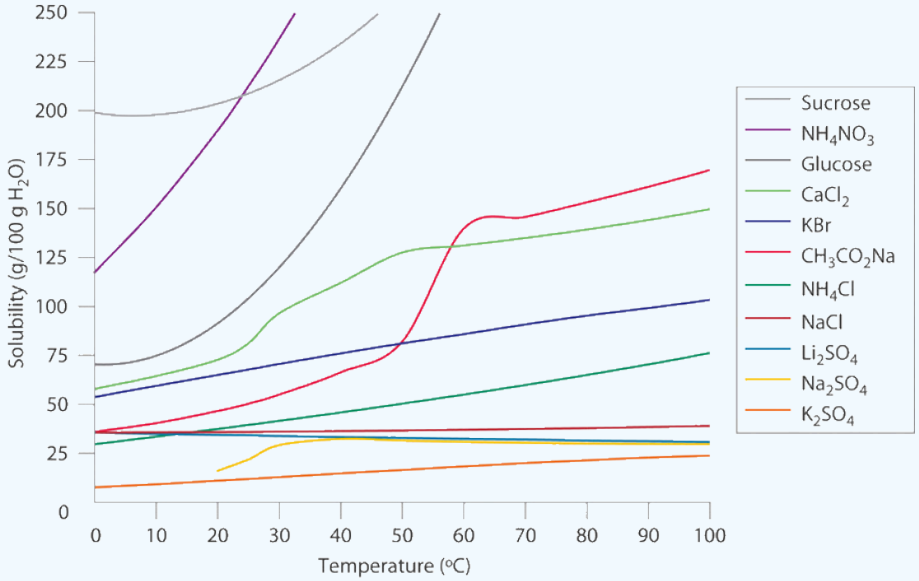
Like K_b, each solvent has a characteristic value of K_f (see Table $4.3.1$). Freezing point depression depends on the total number of dissolved nonvolatile solute particles, just as with boiling point elevation. Thus an aqueous NaCl solution has twice as large a freezing point depression as a glucose solution of the same molality.

People who live in cold climates use freezing point depression to their advantage in many ways. For example, salt is used to melt ice and snow on roads and sidewalks, ethylene glycol is added to engine coolant water to prevent an automobile engine from being destroyed, and methanol is added to windshield washer fluid to prevent the fluid from freezing.

> The decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus a pure liquid all depend on the total number of dissolved nonvolatile solute particles.

Example $4.3.4$: Salting the Roads

In colder regions of the United States, NaCl or $\mathrm{CaCl_2}$ is often sprinkled on icy roads in winter to melt the ice and make driving safer. Use the data in the Figure below to estimate the concentrations of two saturated solutions at 0°C, one of NaCl and one of $\mathrm{CaCl_2}$, and calculate the freezing points of both solutions to see which salt is likely to be more effective at melting ice.



Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature. Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds. (CC BY-NC-SA; anonymous)

Given: solubilities of two compounds

Asked for: concentrations and freezing points

Strategy:

A. Estimate the solubility of each salt in 100 g of water from the figure. Determine the number of moles of each in 100 g and calculate the molalities.
B. Determine the concentrations of the dissolved salts in the solutions. Substitute these values into Equation $4.3.1083$ to calculate the freezing point depressions of the solutions.

Solution:

A. From Figure above, we can estimate the solubilities of NaCl and $\mathrm{CaCl_2}$ to be about 36 g and 60 g, respectively, per 100 g of water at 0°C. The corresponding concentrations in molality are

$$m_{NaCl} = \left(\frac{36\ \cancel{g\ NaCl}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ NaCl}{58.44\ \cancel{g\ NaCl}}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right) = 6.2\ m$$

$$m_{CaCl_2} = \left(\frac{60\ \cancel{g\ CaCl_2}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ CaCl_2}{110.98\ \cancel{g\ CaCl_2}}\right)\left(\frac{1000\ \cancel{g}}{1kg}\right) = 5.4\ m$$

The lower formula mass of NaCl more than compensates for its lower solubility, resulting in a saturated solution that has a slightly higher concentration than $\mathrm{CaCl_2}$.

B. Because these salts are ionic compounds that dissociate in water to yield two and three ions per formula unit of NaCl and $\mathrm{CaCl_2}$, respectively, the actual concentrations of the dissolved species in the two saturated solutions are 2 × 6.2 m = 12 m for NaCl and 3 × 5.4 m = 16 m for $\mathrm{CaCl_2}$. The resulting freezing point depressions can be calculated using Equation 4.3.1083:

$$\mathrm{NaCl}: \Delta T_f = mK_f = (12\ \cancel{m})(1.86°C/\cancel{m}) = 22°C$$

$$\mathrm{CaCl_2}: \Delta T_f = mK_f = (16\ \cancel{m})(1.86°C/\cancel{m}) = 30°C$$

Because the freezing point of pure water is 0°C, the actual freezing points of the solutions are –22°C and –30°C, respectively. Note that $\mathrm{CaCl_2}$ is substantially more effective at lowering the freezing point of water because its solutions contain three ions per formula unit. In fact, $\mathrm{CaCl_2}$ is the salt usually sold for home use, and it is also often used on highways.

Because the solubilities of both salts decrease with decreasing temperature, the freezing point can be depressed by only a certain amount, regardless of how much salt is spread on an icy road. If the temperature is significantly below the minimum temperature at which one of these salts will cause ice to melt (say –35°C), there is no point in using salt until it gets warmer

Exercise 4.3.4

Calculate the freezing point of the 30.2% solution of ethylene glycol in water whose vapor pressure and boiling point we calculated in Examples 4.3.1 and 4.3.3.

Answer

–13.0°C

Example 4.3.5

Arrange these aqueous solutions in order of decreasing freezing points: 0.1 m KCl, 0.1 m glucose, 0.1 m $\mathrm{SrCl_2}$, 0.1 m ethylene glycol, 0.1 m benzoic acid, and 0.1 m HCl.

Given: molalities of six solutions

Asked for: relative freezing points

Strategy:

A. Identify each solute as a strong, weak, or nonelectrolyte, and use this information to determine the number of solute particles produced.
B. Multiply this number by the concentration of the solution to obtain the effective concentration of solute particles. The solution with the highest effective concentration of solute particles has the largest freezing point depression.

Solution:

A Because the molal concentrations of all six solutions are the same, we must focus on which of the substances are strong electrolytes, which are weak electrolytes, and which are nonelectrolytes to determine the actual numbers of particles in solution. KCl, $\mathrm{SrCl_2}$, and HCl are **strong electrolytes**, producing two, three, and two ions per formula unit, respectively. Benzoic acid is a weak electrolyte (approximately one particle per molecule), and glucose and ethylene glycol are both nonelectrolytes (one particle per molecule).

B The molalities of the solutions in terms of the total particles of solute are: KCl and HCl, 0.2 m; $SrCl_2$, 0.3 m; glucose and ethylene glycol, 0.1 m; and benzoic acid, 0.1–0.2 m. Because the magnitude of the decrease in freezing point is proportional to the concentration of dissolved particles, the order of freezing points of the solutions is: glucose and ethylene glycol (highest freezing point, smallest freezing point depression) > benzoic acid > HCl = KCl > $\mathrm{SrCl_2}$.

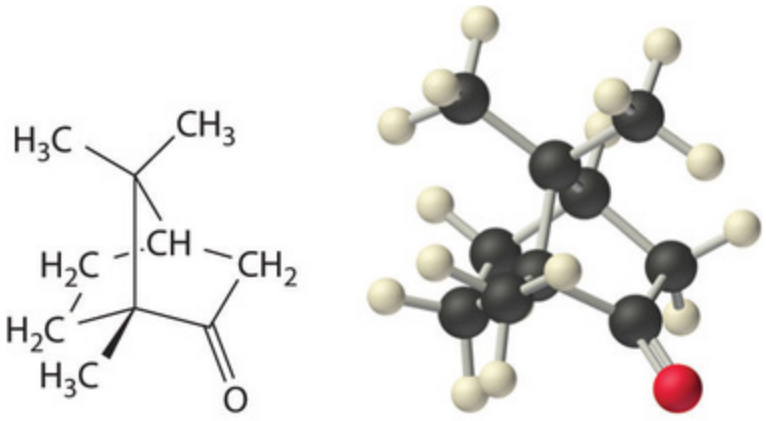
Exercise 4.3.5

Arrange these aqueous solutions in order of increasing freezing points: 0.2 m NaCl, 0.3 m acetic acid, 0.1 m $\mathrm{CaCl_2}$, and 0.2 m sucrose.

Answer

0.2 m NaCl (lowest freezing point) < 0.3 m acetic acid ≈ 0.1 m $\mathrm{CaCl_2}$ < 0.2 m sucrose (highest freezing point)

Colligative properties can also be used to determine the molar mass of an unknown compound. One method that can be carried out in the laboratory with minimal equipment is to measure the freezing point of a solution with a known mass of solute. This method is accurate for dilute solutions (≤1% by mass) because changes in the freezing point are usually large enough to measure accurately and precisely. By comparing K_b and K_f values in Table 4.3.1, we see that changes in the boiling point are smaller than changes in the freezing point for a given solvent. Boiling point elevations are thus more difficult to measure precisely. For this reason, freezing point depression is more commonly used to determine molar mass than is boiling point elevation. Because of its very large value of K_f (37.8°C/m), d-(+)-camphor (Table 4.3.1) is often used to determine the molar mass of organic compounds by this method.



d-(+)-Camphor

Example 4.3.6: Sulfur

A 7.08 g sample of elemental sulfur is dissolved in 75.0 g of CS_2 to create a solution whose freezing point is –113.5°C. Use these data to calculate the molar mass of elemental sulfur and thus the formula of the dissolved S_n molecules (i.e., what is the value of n?).

Given: masses of solute and solvent and freezing point

Asked for: molar mass and number of S atoms per molecule

Strategy:

A. Use Equation 4.3.1082, the measured freezing point of the solution, and the freezing point of CS_2 from Table 4.3.1 to calculate the freezing point depression. Then use Equation 4.3.1083 and the value of K_f from Table 4.3.1 to calculate the molality of the solution.
B. From the calculated molality, determine the number of moles of solute present.
C. Use the mass and number of moles of the solute to calculate the molar mass of sulfur in solution. Divide the result by the molar mass of atomic sulfur to obtain n, the number of sulfur atoms per mole of dissolved sulfur.

Solution:

A The first step is to calculate the freezing point depression using Equation 4.3.1082:

$$\Delta T_f = T_f^0 - T_f = -112.1°C - (-113.5°C) = 1.4°C$$

Then Equation 4.3.1083 gives

$$m = \frac{\Delta T_f}{K_f} = \frac{1.4°\cancel{C}}{3.74°\cancel{C}/m} = 0.37\ m$$

B The total number of moles of solute present in the solution is

$$\text{moles solute} = \left(\frac{0.37 mol}{\cancel{kg}}\right)(75.0\ g)\left(\frac{1 kg}{1000\ g}\right) = 0.028\ mol$$

C We now know that 0.708 g of elemental sulfur corresponds to 0.028 mol of solute. The molar mass of dissolved sulfur is thus

$$\text{molar mass} = \frac{7.08\ g}{0.028\ mol} = 260\ g/mol$$

The molar mass of atomic sulfur is 32 g/mol, so there must be 260/32 = 8.1 sulfur atoms per mole, corresponding to a formula of $\mathrm{S_8}$.

Exercise 4.3.6

One of the byproducts formed during the synthesis of C_{60} is a deep red solid containing only carbon. A solution of 205 mg of this compound in 10.0 g of CCl_4 has a freezing point of –23.38°C. What are the molar mass and most probable formula of the substance?

Answer

847 g/mol; $\mathrm{C_{70}}$

Osmotic Pressure

Osmotic pressure is a colligative property of solutions that is observed using a semipermeable membrane, a barrier with pores small enough to allow solvent molecules to pass through but not solute molecules or ions. The net flow of solvent through a semipermeable membrane is called osmosis (from the Greek osmós, meaning “push”). The direction of net solvent flow is always from the side with the lower concentration of solute to the side with the higher concentration.

Osmosis can be demonstrated using a U-tube like the one shown in Figure 4.3.6, which contains pure water in the left arm and a dilute aqueous solution of glucose in the right arm. A net flow of water through the membrane occurs until the levels in the arms eventually stop changing, which indicates that equilibrium has been reached. The osmotic pressure (Π) of the glucose solution is the difference in the pressure between the two sides, in this case the heights of the two columns. Although the semipermeable membrane allows water molecules to flow through in either direction, the rate of flow is not the same in both directions because the concentration of water is not the same in the two arms. The net flow of water through the membrane can be prevented by applying a pressure to the right arm that is equal to the osmotic pressure of the glucose solution.

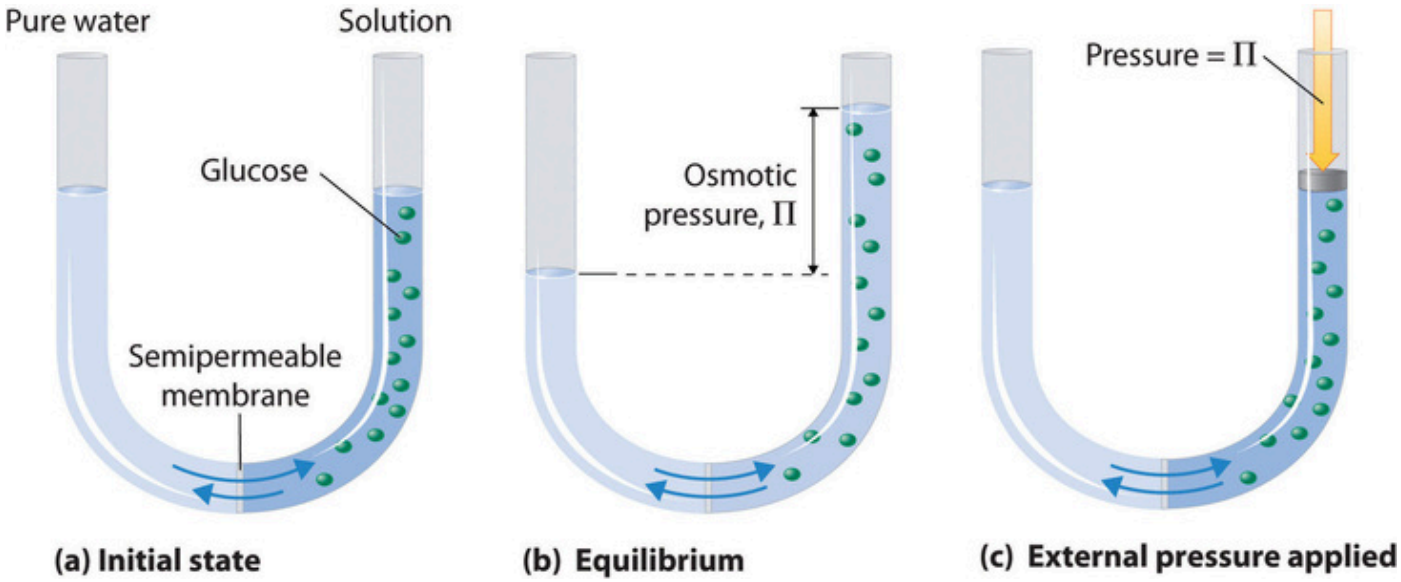


Figure 4.3.6: Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution (Π_{soln}), equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation. (CC BY-NC-SA; anonymous)

Just as with any other colligative property, the osmotic pressure of a solution depends on the concentration of dissolved solute particles. Osmotic pressure obeys a law that resembles the ideal gas equation:

$$\Pi = MRT \tag{4.3.1084}$$

where M is the number of moles of solute per unit volume of solution (i.e., the molarity of the solution), R is the ideal gas constant, and T is the absolute temperature.

As shown in Example 4.3.7, osmotic pressures tend to be quite high, even for rather dilute solutions.

Example 4.3.7

When placed in a concentrated salt solution, certain yeasts are able to produce high internal concentrations of glycerol to counteract the osmotic pressure of the surrounding medium. Suppose that the yeast cells are placed in an aqueous solution containing 4.0% NaCl by mass; the solution density is 1.02 g/mL at 25°C.

a. Calculate the osmotic pressure of a 4.0% aqueous NaCl solution at 25°C.
b. If the normal osmotic pressure inside a yeast cell is 7.3 atm, corresponding to a total concentration of dissolved particles of 0.30 M, what concentration of glycerol must the cells synthesize to exactly balance the external osmotic pressure at 25°C?

Given: concentration, density, and temperature of NaCl solution; internal osmotic pressure of cell

Asked for: osmotic pressure of NaCl solution and concentration of glycerol needed

Strategy:

A. Calculate the molarity of the NaCl solution using the formula mass of the solute and the density of the solution. Then calculate the total concentration of dissolved particles.
B. Use Equation 4.3.1084 to calculate the osmotic pressure of the solution.

C. Subtract the normal osmotic pressure of the cells from the osmotic pressure of the salt solution to obtain the additional pressure needed to balance the two. Use Equation 4.3.1084 to calculate the molarity of glycerol needed to create this osmotic pressure.

Solution:

A The solution contains 4.0 g of NaCl per 100 g of solution. Using the formula mass of NaCl (58.44 g/mol) and the density of the solution (1.02 g/mL), we can calculate the molarity:

$$\begin{aligned} M_{NaCl} &= \frac{moles\ NaCl}{\text{liter solution}} \\ &= \left(\frac{4.0\ \cancel{g}\ NaCl}{58.44\ \cancel{g}/mol\ NaCl}\right)\left(\frac{1}{100\ \cancel{g\ solution}}\right)\left(\frac{1.02\ \cancel{g\ solution}}{1.00\ \cancel{mL}\ solution}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right) \\ &= 0.70\ M\ \mathrm{NaCl} \end{aligned}$$

Because 1 mol of NaCl produces 2 mol of particles in solution, the total concentration of dissolved particles in the solution is (2)(0.70 M) = 1.4 M.

B Now we can use Equation 4.3.1084 to calculate the osmotic pressure of the solution:

$$\begin{aligned} \Pi &= MRT \\ &= (1.4\ mol/L)\,[0.0821\ (L\cdot atm)/(K\cdot mol)]\,(298\ K) \\ &= 34\ atm \end{aligned}$$

C If the yeast cells are to exactly balance the external osmotic pressure, they must produce enough glycerol to give an additional internal pressure of (34 atm – 7.3 atm) = 27 atm. Glycerol is a nonelectrolyte, so we can solve Equation 4.3.1084 for the molarity corresponding to this osmotic pressure:

$$\begin{aligned} M &= \frac{\Pi}{RT} \\ &= \frac{27\ \cancel{atm}}{[0.0821(L\cdot \cancel{atm})/(\cancel{K}\cdot mol)](298\ \cancel{K})} \\ &= 1.1\ M\ \text{glycerol} \end{aligned}$$

In solving this problem, we could also have recognized that the only way the osmotic pressures can be the same inside the cells and in the solution is if the concentrations of dissolved particles are the same. We are given that the normal concentration of dissolved particles in the cells is 0.3 M, and we have calculated that the NaCl solution is effectively 1.4 M in dissolved particles. The yeast cells must therefore synthesize enough glycerol to increase the internal concentration of dissolved particles from 0.3 M to 1.4 M—that is, an additional 1.1 M concentration of glycerol.

Exercise 4.3.7

Assume that the fluids inside a sausage are approximately 0.80 M in dissolved particles due to the salt and sodium nitrite used to prepare them. Calculate the osmotic pressure inside the sausage at 100°C to learn why experienced cooks pierce the semipermeable skin of sausages before boiling them.

Answer

24 atm

Because of the large magnitude of osmotic pressures, osmosis is extraordinarily important in biochemistry, biology, and medicine. Virtually every barrier that separates an organism or cell from its environment acts like a semipermeable membrane, permitting the flow of water but not solutes. The same is true of the compartments inside an organism or cell. Some specialized barriers, such as those in your kidneys, are slightly more permeable and use a related process called dialysis, which permits both water and small molecules to pass through but not large molecules such as proteins.

The same principle has long been used to preserve fruits and their essential vitamins over the long winter. High concentrations of sugar are used in jams and jellies not for sweetness alone but because they greatly increase the osmotic pressure. Thus any bacteria not killed in the cooking process are dehydrated, which keeps them from multiplying in an otherwise rich medium for bacterial growth. A similar process using salt prevents bacteria from growing in ham, bacon, salt pork, salt cod, and other preserved meats. The effect of osmotic pressure is dramatically illustrated in Figure 4.3.7, which shows what happens when red blood cells are placed in a solution whose osmotic pressure is much lower or much higher than the internal pressure of the cells.

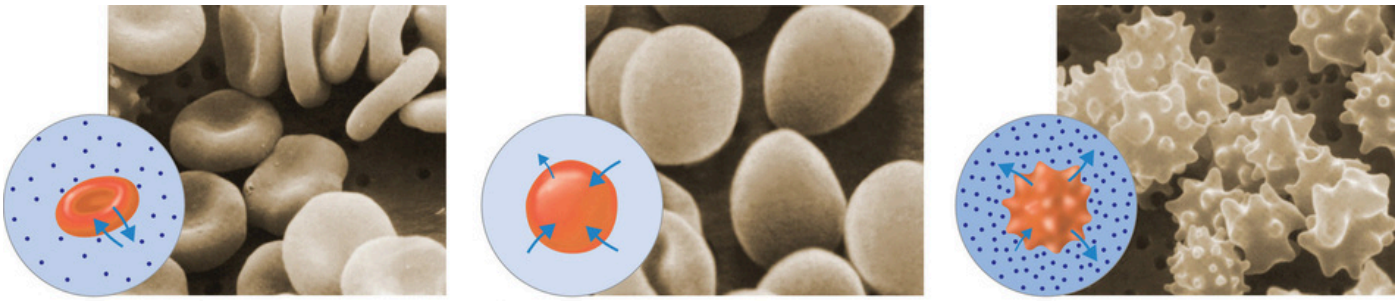


Figure 4.3.7: Effect on Red Blood Cells of the Surrounding Solution's Osmotic Pressure. (a) When red blood cells are placed in a dilute salt solution having the same osmotic pressure as the intracellular fluid, the rate of flow of water into and out of the cells is the same and their shape does not change. (b) When cells are placed in distilled water whose osmotic pressure is less than that of the intracellular fluid, the rate of flow of water into the cells is greater than the rate of flow out of the cells. The cells swell and eventually burst. (c) When cells are placed in a concentrated salt solution with an osmotic pressure greater than that of the intracellular fluid, the rate of flow of water out of the cells is greater than the rate of flow into the cells. The cells shrivel and become so deformed that they cannot function. (CC BY-NC-SA; anonymous)

In addition to capillary action, trees use osmotic pressure to transport water and other nutrients from the roots to the upper branches. Evaporation of water from the leaves results in a local increase in the salt concentration, which generates an osmotic pressure that pulls water up the trunk of the tree to the leaves.

Finally, a process called reverse osmosis can be used to produce pure water from seawater. As shown schematically in Figure 4.3.8, applying high pressure to seawater forces water molecules to flow through a semipermeable membrane that separates pure water from the solution, leaving the dissolved salt behind. Large-scale desalinization plants that can produce hundreds of thousands of gallons of freshwater per day are common in the desert lands of the Middle East, where they supply a large proportion of the freshwater needed by the population. Similar facilities are now being used to supply freshwater in southern California. Small, hand-operated reverse osmosis units can produce approximately 5 L of freshwater per hour, enough to keep 25 people alive, and are now standard equipment on US Navy lifeboats.

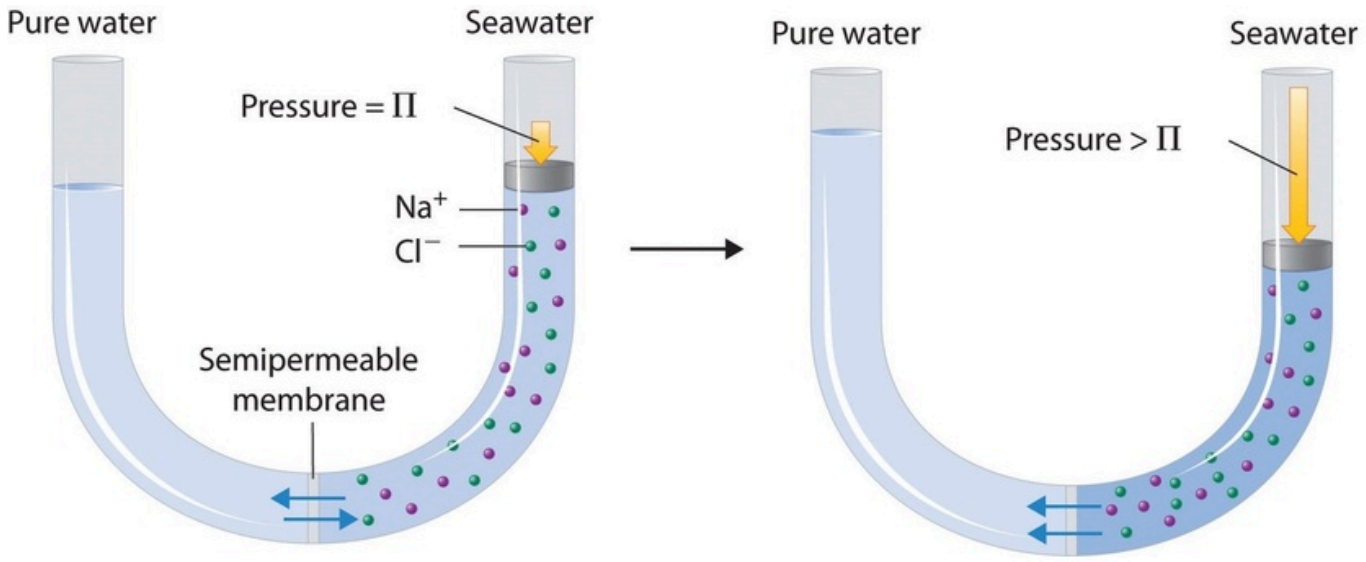


Figure 4.3.8: Desalinization of Seawater by Reverse Osmosis. (top) When the pressure applied to seawater equals its osmotic pressure (Π_{soln}), there is no net flow of water across the semipermeable membrane. (bottom) The application of pressure greater than the osmotic pressure of seawater forces water molecules to flow through the membrane, leaving behind a concentrated salt solution. In desalinization plants, seawater is continuously introduced under pressure and pure water is collected, so the process continues indefinitely. (CC BY-NC-SA; anonymous)

Colligative Properties of Electrolyte Solutions

Thus far we have assumed that we could simply multiply the molar concentration of a solute by the number of ions per formula unit to obtain the actual concentration of dissolved particles in an electrolyte solution. We have used this simple model to predict such properties as freezing points, melting points, vapor pressure, and osmotic pressure. If this model were perfectly correct, we would expect the freezing point depression of a 0.10 m solution of sodium chloride, with 2 mol of ions per mole of NaCl in solution, to be exactly twice that of a 0.10 m solution of glucose, with only 1 mol of molecules per mole of glucose in solution. In reality, this is not always the case. Instead, the observed change in freezing points for 0.10 m aqueous solutions of NaCl and KCl are significantly less than expected (−0.348°C and −0.344°C, respectively, rather than −0.372°C), which suggests that fewer particles than we expected are present in solution.

The relationship between the actual number of moles of solute added to form a solution and the apparent number as determined by colligative properties is called the van 't Hoff factor (i) and is defined as follows:

[redacted]

Named for Jacobus Hendricus van 't Hoff (1852–1911), a Dutch chemistry professor at the University of Amsterdam who won the first Nobel Prize in Chemistry (1901) for his work on thermodynamics and solutions.

As the solute concentration increases, the van 't Hoff factor decreases.

The van 't Hoff factor is therefore **a measure of a deviation from ideal behavior**. The lower the van 't Hoff factor, the greater the deviation. As the data in Table 4.3.2 show, the van 't Hoff factors for ionic compounds are somewhat lower than expected; that is, their solutions apparently contain fewer particles than predicted by the number of ions per formula unit. As the concentration of the solute increases, the van 't Hoff factor decreases because ionic compounds generally do not totally dissociate in aqueous solution.

Table 4.3.2: van 't Hoff Factors for 0.0500 M Aqueous Solutions of Selected Compounds at 25°C

Compound	i (measured)	i (ideal)
glucose	1.0	1.0
sucrose	1.0	1.0

Compound	i (measured)	i (ideal)
$NaCl$	1.9	2.0
HCl	1.9	2.0
$MgCl_2$	2.7	3.0
$FeCl_3$	3.4	4.0
$Ca(NO_3)_2$	2.5	3.0
$AlCl_3$	3.2	4.0
$MgSO_4$	1.4	2.0

Instead, some of the ions exist as ion pairs, a cation and an anion that for a brief time are associated with each other without an intervening shell of water molecules (Figure 4.3.9). Each of these temporary units behaves like a single dissolved particle until it dissociates. Highly charged ions such as Mg^{2+}, Al^{3+}, SO_4^{2-}, and PO_4^{3-} have a greater tendency to form ion pairs because of their strong electrostatic interactions. The actual number of solvated ions present in a solution can be determined by measuring a colligative property at several solute concentrations.

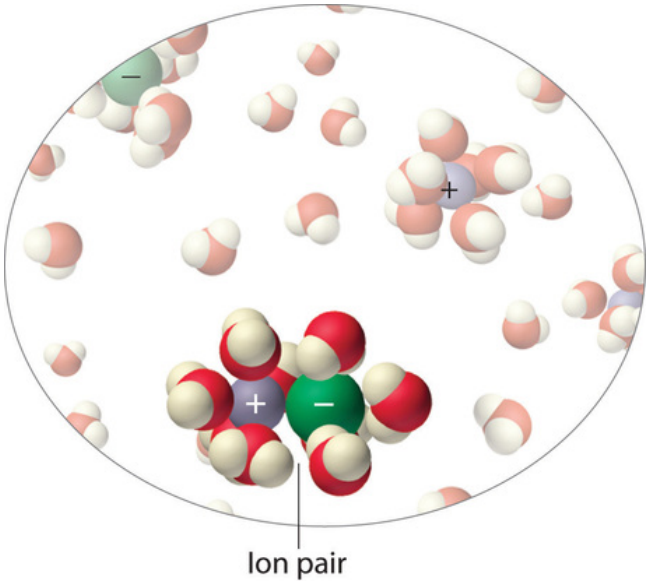


Figure 4.3.9: Ion Pairs. In concentrated solutions of electrolytes like $NaCl$, some of the ions form neutral ion pairs that are not separated by solvent and diffuse as single particles.

Example 4.3.8: Iron Chloride in Water

A 0.0500 M aqueous solution of $\mathrm{FeCl_3}$ has an osmotic pressure of 4.15 atm at 25°C. Calculate the van 't Hoff factor i for the solution.

Given: solute concentration, osmotic pressure, and temperature

Asked for: van 't Hoff factor

Strategy:

A. Use Equation 4.3.1084 to calculate the expected osmotic pressure of the solution based on the effective concentration of dissolved particles in the solvent.
B. Calculate the ratio of the observed osmotic pressure to the expected value. Multiply this number by the number of ions of solute per formula unit, and then use Equation 4.3.1085 to calculate the van 't Hoff factor.

Solution:

A If $\mathrm{FeCl_3}$ dissociated completely in aqueous solution, it would produce four ions per formula unit (one $\mathrm{Fe^{3+}(aq)}$ and three \(\ce{Cl^{-}(aq)} ions) for an effective concentration of dissolved particles of 4 × 0.0500 M = 0.200 M. The osmotic pressure would be

$$\begin{aligned}\Pi &= MRT \\ &= (0.200\ mol/L)\,[0.0821\ (L\cdot atm)/(K\cdot mol)]\,(298\ K) = 4.89\ atm\end{aligned}$$

B The observed osmotic pressure is only 4.15 atm, presumably due to ion pair formation. The ratio of the observed osmotic pressure to the calculated value is 4.15 atm/4.89 atm = 0.849, which indicates that the solution contains (0.849)(4) = 3.40 moles of particles per mole of $\mathrm{FeCl_3}$ dissolved. Alternatively, we can calculate the observed particle concentration from the osmotic pressure of 4.15 atm:

$$4.15\ atm = M\left(\frac{0.0821\ (L\cdot atm)}{(K\cdot mol)}\right)(298\ K)$$

or after rearranging

$$M = 0.170 mol$$

The ratio of this value to the expected value of 0.200 M is 0.170 M/0.200 M = 0.850, which again gives us (0.850)(4) = 3.40 mole of particles per mole of $\mathrm{FeCl_3}$ dissolved. From Equation 4.3.1085, the van 't Hoff factor for the solution is

$$i = \frac{3.40\ \text{particles observed}}{1\ \text{formula unit}\ \mathrm{FeCl_3}} = 3.40$$

Exercise 4.3.8: Magnesium Chloride in Water

Calculate the van 't Hoff factor for a 0.050 m aqueous solution of $\mathrm{MgCl_2}$ that has a measured freezing point of −0.25°C.

Answer

2.7 (versus an ideal value of 3).

Summary

The colligative properties of a solution depend on only the total number of dissolved particles in solution, not on their chemical identity. Colligative properties include vapor pressure, boiling point, freezing point, and osmotic pressure. The addition of a nonvolatile solute (one without a measurable vapor pressure) decreases the vapor pressure of the solvent. The vapor pressure of the solution is proportional to the mole fraction of solvent in the solution, a relationship known as **Raoult's law**. The boiling point elevation (ΔT_b) and freezing point depression (ΔT_f) of a solution are defined as the differences between the boiling and freezing points, respectively, of the solution and the pure solvent. Both are proportional to the molality of the solute. When a solution and a pure solvent are separated by a semipermeable membrane, a barrier that allows solvent molecules but not solute molecules to pass through, the flow of solvent in opposing directions is unequal and produces an osmotic pressure, which is the difference in pressure between the two sides of the membrane. Osmosis is the net flow of solvent through such a membrane due to different solute concentrations. Dialysis uses a semipermeable membrane with pores that allow only small solute molecules and solvent molecules to pass through. In more concentrated solutions, or in solutions of salts with highly charged ions, the cations and anions can associate to form ion pairs, which decreases their effect on the colligative properties of the solution. The extent of ion pair formation is given by the van 't Hoff factor (i), the ratio of the apparent number of particles in solution to the number predicted by the stoichiometry of the salt.

- **Henry's law:**

$$C = kP$$

- **Raoult's law**:

$$P_A = \chi_A P_A^0$$

- **vapor pressure lowering**:

$$P_A^0 - P_A = \Delta P_A = \chi_B P_A^0$$

- **vapor pressure of a system containing two volatile components**:

$$P_{tot} = \chi_A P_A^0 + (1 - \chi_A) P_B^0$$

- **boiling point elevation**:

$$\Delta T_b = mK_b$$

- **freezing point depression:**

$$\Delta T_f = mK_f$$

- **osmotic pressure**:

$$\Pi = \frac{n}{V} RT = MRT$$

- **van 't Hoff factor**:

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}}$$

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4.4: Phase Equilibrium in Solutions - Volatile Solutes

Learning Objectives

- To understand the relationship among temperature, pressure, and solubility.
- The understand that the solubility of a solid may increase or decrease with increasing temperature,
- To understand that the solubility of a gas decreases with an increase in temperature and a decrease in pressure.
- Describe the physical reasons that a binary liquid solution might exhibit non-ideal behavior

Vapor Pressure of Solutions and Raoult's Law For Volatile Solutes

When a solute is volatile, meaning that it has a measurable vapor pressure, we can still use Raoult's law. In this case, we calculate the vapor pressure of each component separately. The total vapor pressure of the solution (P_{tot}) is the sum of the vapor pressures of the components:

[redacted]

Because $\chi_B = 1 - \chi_A$ for a two-component system,

[redacted]

Thus we need to specify the mole fraction of only one of the components in a two-component system. Consider, for example, the vapor pressure of solutions of benzene and toluene of various compositions. At 20°C, the vapor pressures of pure benzene and toluene are 74.7 and 22.3 mmHg, respectively. The vapor pressure of benzene in a benzene–toluene solution is

[redacted]

and the vapor pressure of toluene in the solution is

[redacted]

Equations 4.4.1089 and 4.4.1090 are both in the form of the equation for a straight line: $y = mx + b$, where $b = 0$. Plots of the vapor pressures of both components versus the mole fractions are therefore straight lines that pass through the origin, as shown in Figure 4.4.3. Furthermore, a plot of the total vapor pressure of the solution versus the mole fraction is a straight line that represents the sum of the vapor pressures of the pure components. Thus the vapor pressure of the solution is always greater than the vapor pressure of either component.

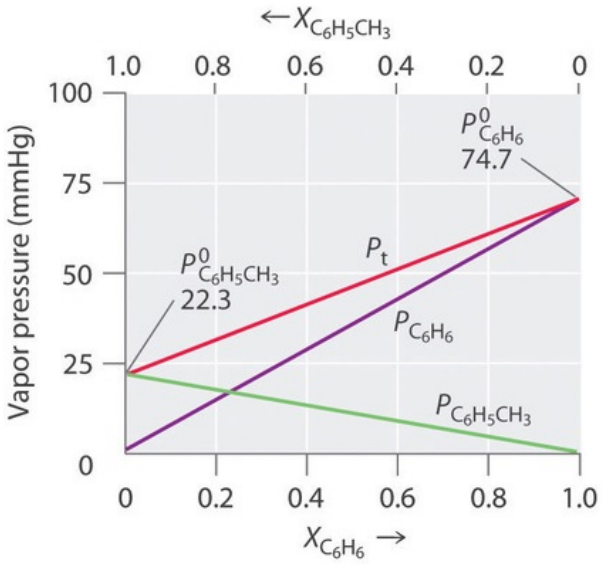


Figure 4.4.1: Vapor Pressures of Benzene–Toluene Solutions. Plots of the vapor pressures of benzene (C_6H_6) and toluene ($C_6H_5CH_3$) versus the mole fractions at 20°C are straight lines. For a solution like this, which approximates an ideal solution, the total vapor pressure of the solution (P_{tot}) is the sum of the vapor pressures of the components. (CC BY-NS-SA 4.0; Anonymous via LibreTexts).

A solution of two volatile components that behaves like the solution in Figure 4.4.3, which is defined as a solution that obeys Raoult's law. Like an ideal gas, an ideal solution is a hypothetical system whose properties can be described in terms of a simple model. Mixtures of benzene and toluene approximate an ideal solution because the intermolecular forces in the two pure liquids are almost identical in both kind and magnitude. Consequently, the change in enthalpy on solution formation is essentially zero ($\Delta H_{soln} \approx 0$), which is one of the defining characteristics of an ideal solution.

> Ideal solutions and ideal gases are both simple models that ignore intermolecular interactions.

Example 4.4.1

For each system, compare the intermolecular interactions in the pure liquids and in the solution to decide whether the vapor pressure will be greater than that predicted by Raoult's law (positive deviation), approximately equal to that predicted by Raoult's law (an ideal solution), or less than the pressure predicted by Raoult's law (negative deviation).

a. cyclohexane and ethanol
b. methanol and acetone
c. n-hexane and isooctane (2,2,4-trimethylpentane)

Given: identity of pure liquids

Asked for: predicted deviation from Raoult's law (Equation 4.4.1087)

Strategy:

Identify whether each liquid is polar or nonpolar, and then predict the type of intermolecular interactions that occur in solution.

Solution:

a. Liquid ethanol contains an extensive hydrogen bonding network, and cyclohexane is nonpolar. Because the cyclohexane molecules cannot interact favorably with the polar ethanol molecules, they will disrupt the hydrogen bonding. Hence the A–B interactions will be weaker than the A–A and B–B interactions, leading to a higher vapor pressure than predicted by Raoult's law (a positive deviation).
b. Methanol contains an extensive hydrogen bonding network, but in this case the polar acetone molecules create A–B interactions that are stronger than the A–A or B–B interactions, leading to a negative enthalpy of solution and a lower vapor pressure than predicted by Raoult's law (a negative deviation).
c. Hexane and isooctane are both nonpolar molecules (isooctane actually has a very small dipole moment, but it is so small that it can be ignored). Hence the predominant intermolecular forces in both liquids are London dispersion forces. We expect the A–B interactions to be comparable in strength to the A–A and B–B interactions, leading to a vapor pressure in good agreement with that predicted by Raoult's law (an ideal solution).

Exercise 4.4.1

For each system, compare the intermolecular interactions in the pure liquids with those in the solution to decide whether the vapor pressure will be greater than that predicted by Raoult's law (positive deviation), approximately equal to that predicted by Raoult's law (an ideal solution), or less than the pressure predicted by Raoult's law (negative deviation):

a. benzene and n-hexane
b. ethylene glycol and $\mathrm{CCl_4}$
c. acetic acid and n-propanol

Answer a

approximately equal

Answer b

positive deviation (vapor pressure greater than predicted)

Answer c

negative deviation (vapor pressure less than predicted)

Ideal vs. Real Solutions

Another solution whose components follow Raoult's law quite closely is a solution of hexane $\mathrm{C_6H_{14}}$ and heptane $\mathrm{C_7H_{16}}$. The total vapor pressure of this solution varies in a straight-line manner with the mole fraction composition of the mixture (Figure 4.4.2). Note that the mole fraction scales at the top and bottom run in opposite directions, since by definition,

$$\chi_{hexane} = 1 - \chi_{heptane}$$

If this solution behaves ideally, then is the sum of the Raoult's law plots for the two pure compounds (i.e., Equation 4.4.1086):

$$P_{total} = P_{heptane} + P_{hexane}$$

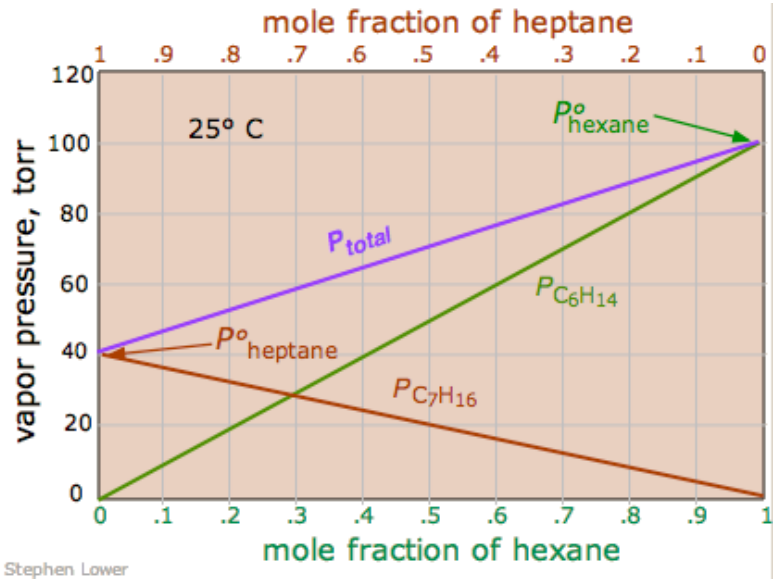
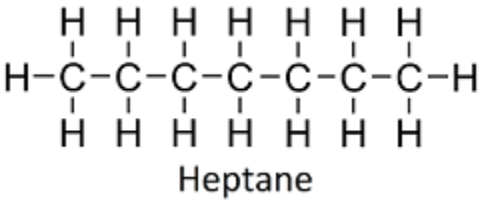
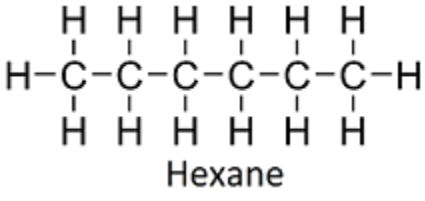


Figure 4.4.2: Raoult's law plot for a mixture of hexane and heptane. (CC BY 4.0; Stephen Lower via Chem1).

An *ideal solution* is one whose vapor pressure follows Raoult's law throughout its range of compositions. Experience has shown solutions that approximate ideal behavior are composed of molecules having very similar structures. Thus hexane and heptane are both linear hydrocarbons that differ only by a single $-CH_2$ group.





Most real solutions, however, do not obey Raoult's law precisely, just as most real gases do not obey the ideal gas law exactly. Real solutions generally deviate from Raoult's law because the intermolecular interactions between the two components A and B differ. We can distinguish between two general kinds of behavior, depending on whether the intermolecular interactions between molecules A and B are stronger or weaker than the A–A and B–B interactions in the pure components.

- If the A–B interactions are *stronger* than the A–A and B–B interactions, each component of the solution exhibits a lower vapor pressure than expected for an ideal solution, as does the solution as a whole. The favorable A–B interactions effectively stabilize the solution compared with the vapor. This kind of behavior is called a negative deviation from Raoult's law. Systems stabilized by hydrogen bonding between two molecules, such as acetone and ethanol, exhibit **negative deviations** from Raoult's law. The chloroform-acetone system (Figure 4.4.3) is a good example.
- Conversely, if the A–B interactions are *weaker* than the A–A and B–B interactions yet the entropy increase is enough to allow the solution to form, both A and B have an increased tendency to escape from the solution into the vapor phase. The result is a higher vapor pressure than expected for an ideal solution, producing a **positive deviation** from Raoult's law. In a solution of CCl_4 and methanol, for example, the nonpolar CCl_4 molecules interrupt the extensive hydrogen bonding network in methanol, and the lighter methanol molecules have weaker London dispersion forces than the heavier CCl_4 molecules. Consequently, solutions of CCl_4 and methanol exhibit **positive deviations** from Raoult's law. It should not be surprising molecules as different as benzene and CS_2 should interact more strongly with their own kind, hence the positive deviation in Figure 4.4.3).

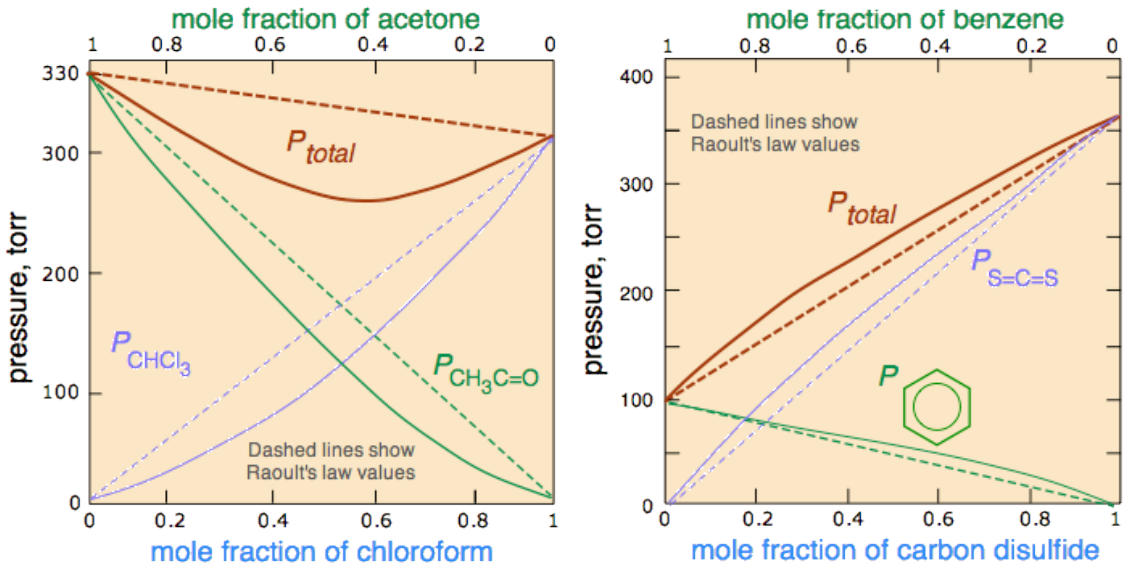


Figure 4.4.3: Systems with negative deviation (left) and positive deviation (right) of Raoult's law. (CC BY 4.0; Stephen Lower via Chem1)

Ideal Solutions vs. Ideal Gases

The ideal solution differs in a fundamental way from the definition of an ideal gas, defined as a hypothetical substance that follows the ideal gas law. The kinetic molecular theory that explains ideal gas behavior assumes that the molecules occupy no space and that intermolecular attractions are totally absent.

The definition of an ideal gas is clearly inapplicable to liquids, whose volumes directly reflect the volumes of their component molecules. And of course, the very ability of the molecules to form a condensed phase is due to the attractive forces between the molecules. So the most we can say about an ideal solution is that the attractions between its all of its molecules are identical — that is, A-type molecules are as strongly attracted to other A molecules as to B-type molecules. Ideal solutions are perfectly democratic: there are no favorites.

You will recall that all gases approach ideal behavior as their pressures approach zero. In the same way, as the mole fraction of either component approaches unity, the behavior of the solution approaches ideality. This is a simple consequence of the fact that at these limits, each molecule is surrounded mainly by its own kind, and the few A-B interactions will have little effect. Raoult's law is therefore a limiting law:

$$P_i = \lim_{x_i \to 0} P^o \chi_i \tag{4.4.1543}$$

it gives the partial pressure of a substance in equilibrium with the solution more and more closely as the mole fraction of that substance approaches unity.

Effect of Pressure on the Solubility of Gases - Henry's Law

External pressure has very little effect on the solubility of liquids and solids. In contrast, the solubility of gases increases as the partial pressure of the gas above a solution increases. This point is illustrated in Figure 4.4.4, which shows the effect of increased pressure on the dynamic equilibrium that is established between the dissolved gas molecules in solution and the molecules in the gas phase above the solution. Because the concentration of molecules in the gas phase increases with increasing pressure, the concentration of dissolved gas molecules in the solution at equilibrium is also higher at higher pressures.

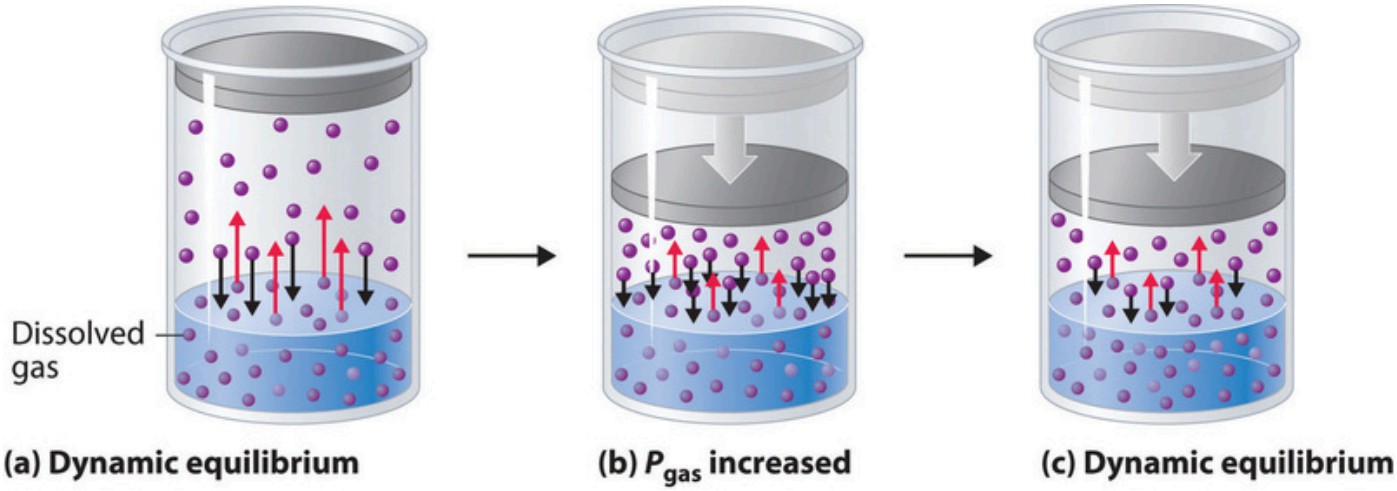


Figure 4.4.4: A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature. (a) When a gas comes in contact with a pure liquid, some of the gas molecules (purple spheres) collide with the surface of the liquid and dissolve. When the concentration of dissolved gas molecules has increased so that the rate at which gas molecules escape into the gas phase is the same as the rate at which they dissolve, a dynamic equilibrium has been established, as depicted here. This equilibrium is entirely analogous to the one that maintains the vapor pressure of a liquid. (b) Increasing the pressure of the gas increases the number of molecules of gas per unit volume, which increases the rate at which gas molecules collide with the surface of the liquid and dissolve. (c) As additional gas molecules dissolve at the higher pressure, the concentration of dissolved gas increases until a new dynamic equilibrium is established.

The relationship between pressure and the solubility of a gas is described quantitatively by Henry's law, which is named for its discoverer, the English physician and chemist, William Henry (1775–1836):

[redacted]

where C is the concentration of dissolved gas at equilibrium, P is the partial pressure of the gas, and k_H is the Henry's law constant, which must be determined experimentally for each combination of gas, solvent, and temperature.

Although the gas concentration may be expressed in any convenient units, we will use molarity exclusively. The units of the Henry's law constant are therefore mol/(L·atm) = M/atm. Values of the Henry's law constants for solutions of several gases in water at 20°C are listed in Table 4.4.1.

As the data in Table 4.4.1 demonstrate, the concentration of a dissolved gas in water at a given pressure depends strongly on its physical properties. For a series of related substances, London dispersion forces increase as molecular mass increases. Thus among the Group 18 elements, the Henry's law constants increase smoothly from He to Ne to Ar.

Table 4.4.1: Henry's Law Constants for Selected Gases in Water at 20°C

Gas	Henry's Law Constant [mol/(L·atm)] × 10^{-4}
He	3.9
Ne	4.7
Ar	15
$\mathrm{H_2}$	8.1
$\mathrm{N_2}$	7.1
$\mathrm{O_2}$	14
$\mathrm{CO_2}$	392

Oxygen is Especially Soluble

Nitrogen and oxygen are the two most prominent gases in the Earth's atmosphere and they share many similar physical properties. However, as Table $4.4.1$ shows, O_2 is twice as soluble in water as N_2. Many factors contribute to solubility including the nature of the intermolecular forces at play. For a details discussion, see "The O_2/N_2 Ratio Gas Solubility Mystery" by Rubin Battino and Paul G. Seybold (J. Chem. Eng. Data 2011, 56, 5036–5044),

Gases that react chemically with water, such as HCl and the other hydrogen halides, H_2S, and NH_3, do **not** obey Henry's law; all of these gases are much more soluble than predicted by Henry's law. For example, HCl reacts with water to give $H^+(aq)$ and $Cl^-(aq)$, not dissolved HCl molecules, and its dissociation into ions results in a much higher solubility than expected for a neutral molecule.

> Gases that *react* with water do not obey Henry's law.

Henry's law has important applications. For example, bubbles of CO_2 form as soon as a carbonated beverage is opened because the drink was bottled under CO_2 at a pressure greater than 1 atm. When the bottle is opened, the pressure of CO_2 above the solution drops rapidly, and some of the dissolved gas escapes from the solution as bubbles. Henry's law also explains why scuba divers have to be careful to ascend to the surface slowly after a dive if they are breathing compressed air. At the higher pressures under water, more N2 from the air dissolves in the diver's internal fluids. If the diver ascends too quickly, the rapid pressure change causes small bubbles of N_2 to form throughout the body, a condition known as "the bends." These bubbles can block the flow of blood through the small blood vessels, causing great pain and even proving fatal in some cases.

Due to the low Henry's law constant for O_2 in water, the levels of dissolved oxygen in water are too low to support the energy needs of multicellular organisms, including humans. To increase the O_2 concentration in internal fluids, organisms synthesize highly soluble carrier molecules that bind O_2 reversibly. For example, human red blood cells contain a protein called hemoglobin that specifically binds O_2 and facilitates its transport from the lungs to the tissues, where it is used to oxidize food molecules to provide energy. The concentration of hemoglobin in normal blood is about 2.2 mM, and each hemoglobin molecule can bind four O_2 molecules. Although the concentration of dissolved O_2 in blood serum at 37°C (normal body temperature) is only 0.010 mM, the total dissolved O_2 concentration is 8.8 mM, almost a thousand times greater than would be possible without hemoglobin. Synthetic oxygen carriers based on fluorinated alkanes have been developed for use as an emergency replacement for whole blood. Unlike donated blood, these "blood substitutes" do not require refrigeration and have a long shelf life. Their very high Henry's law constants for O_2 result in dissolved oxygen concentrations comparable to those in normal blood.

Example $4.4.2$: Oxygen in Water

The Henry's law constant for O_2 in water at 25°C is $1.27 \times 10^{-3} M/atm$, and the mole fraction of O_2 in the atmosphere is 0.21. Calculate the solubility of O_2 in water at 25°C at an atmospheric pressure of 1.00 atm.

Given: Henry's law constant, mole fraction of O_2, and pressure

Asked for: solubility

Strategy:

A. Use Dalton's law of partial pressures to calculate the partial pressure of oxygen.
B. Use Henry's law (Equation $4.4.1092$) to calculate the solubility, expressed as the concentration of dissolved gas.

Solution:

A According to Dalton's law, the partial pressure of O_2 is proportional to the mole fraction of O_2:

$$P_A = \chi_A P_t = (0.21)(1.00\ atm) = 0.21\ atm$$

B From Henry's law, the concentration of dissolved oxygen under these conditions is

$$[\mathrm{CO_2}] = k_H P_{O_2} = (1.27 \times 10^{-3}\ M/\cancel{atm})(0.21\ \cancel{atm}) = 2.7 \times 10^{-4}\ M$$

Exercise 4.4.2: Carbon Dioxide in Water

To understand why soft drinks "fizz" and then go "flat" after being opened, calculate the concentration of dissolved CO_2 in a soft drink:

a. bottled under a pressure of 5.0 atm of CO_2
b. in equilibrium with the normal partial pressure of CO_2 in the atmosphere (approximately $3 \times 10^{-4}\ atm$). The Henry's law constant for CO_2 in water at 25°C is $3.4 \times 10^{-2}\ M/atm$.

Answer a

0.17 M

Answer b

$1 \times 10^{-5} M$

Summary

The vapor pressure of the solution with volatile solute and solvent is proportional to the mole fraction of solute and solvent in the solution, via a modified version of Raoult's law discussed previously. Solutions that obey Raoult's law are called ideal solutions. Most real solutions exhibit positive or negative deviations from Raoult's law. In an ideal solution, the interactions are there, but they are all energetically identical. Thus in an ideal solution of molecules A and B, A—A and B—B attractions are the same as A—B attractions. This is the case only when the two components are chemically and structurally very similar.

The solubility of most substances depends strongly on the temperature and, in the case of gases, on the pressure. The solubility of most solid or liquid solutes increases with increasing temperature. The components of a mixture can often be separated using fractional crystallization, which separates compounds according to their solubilities. The solubility of a gas decreases with increasing temperature. Henry's law describes the relationship between the pressure and the solubility of a gas.

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4.5: Separating Volatile Solutions - Distillation

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- Sketch out a typical *boiling point diagram* for a binary liquid solution, and use this to show how a simple one-stage *distillation* works.
- Explain the role of the *lever rule* in fractional distillation
- Describe the purpose and function of a *fractionating column*
- Sketch out boiling point diagrams for high- and low-boiling *azeotropes*
- Describe the role of distillation in *crude oil refining*, and explain, in a very general way, how further processing is used to increase the yield of gasoline motor fuel.

Distillation is a process whereby a mixture of liquids having different vapor pressures is separated into its components. At first one might think that this would be quite simple: if you have a solution consisting of liquid A that boils at 50°C and liquid B with a boiling point of 90°C, all that would be necessary would be to heat the mixture to some temperature between these two values; this would boil off all the A (whose vapor could then be condensed back into pure liquid A), leaving pure liquid B in the pot. But that overlooks that fact that these liquids will have substantial vapor pressures at *all* temperatures, not only at their boiling points.

Vapor Pressure vs. Composition Phase Diagrams

To fully understand distillation, we will consider an ideal binary liquid mixture of A and B. If the mole fraction of A in the mixture is χ_A, then by the definition of mole fraction, that of B is

$$\chi_B = 1 - \chi_A \tag{4.5.1544}$$

Since distillation depends on the different vapor pressures of the components to be separated, let's first consider the vapor pressure vs. composition plots (Figure 4.5.1) for a hypothetical mixture at some arbitrary temperature at which both liquid and gas phases can exist, depending on the total pressure.

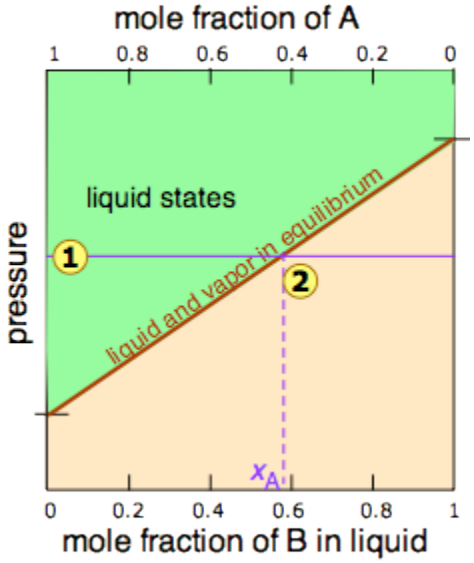


Figure 4.5.1: Liquid-Vapor Equilibrium curve.

In Figure 4.5.2, all states of the system (i.e., combinations of pressure and composition) in which the solution exists solely as a **liquid** are shaded in green. Since liquids are more stable at higher pressures, these states occupy the upper part of the diagram. At any given total vapor pressure such as at (1), the composition of the vapor in equilibrium with the liquid (designated by x_A) corresponds to the intercept with the diagonal equilibrium line at (2). The diagonal line is just an expression of the linearity between vapor pressure and composition according to Raoult's law.

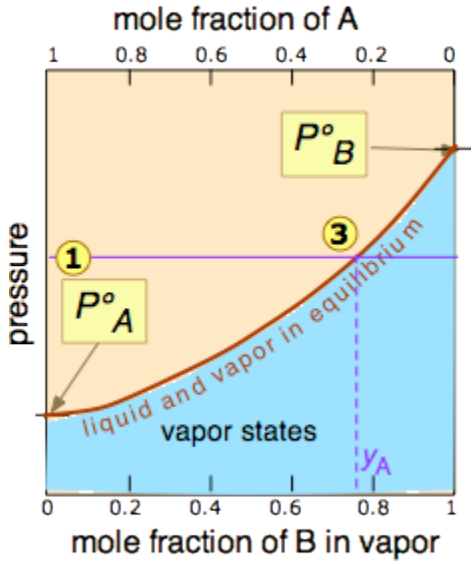


Figure 4.5.2: Liquid-Vapor Equilibrium curve. (3) of the pressure line (1) with the equilibrium curve defines the mole fractions of A and B present in the vapor. (Note that mole fractions of gases, which we are dealing with here, are conventionally represented by y, hence y_A and y_B). The curvature of the equilibrium line arises from the need to combine Raoult's law with Dalton's law of partial pressures which applies to gaseous mixtures. Figure 4.5.3.

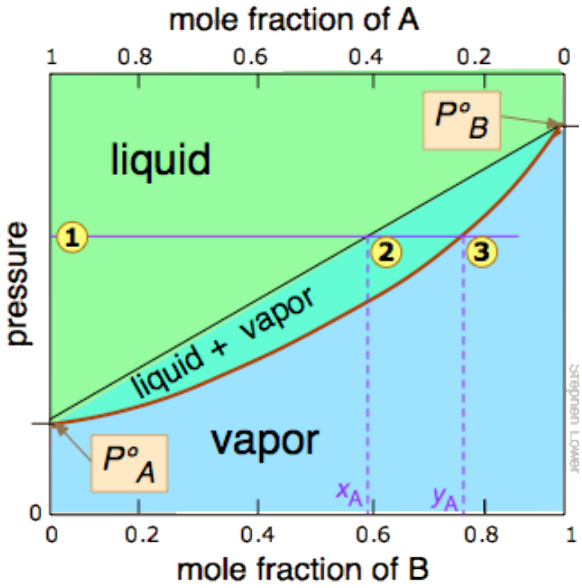


Figure 4.5.3

The two liquid-vapor equilibrium lines (one curved, the other straight) now enclose an area in which liquid and vapor can **coexist**; outside of this region, the mixture will consist entirely of liquid or of vapor. At this particular pressure (1), the intercept (2) with the upper boundary of the two-phase region gives the mole fractions of A and B in the liquid phase, while the intercept (3) with the lower boundary gives the mole fractions of the two components in the vapor.

Exercise 4.5.1

Take a moment to study Figure 4.5.5 and to confirm that

- because both intercepts occur on equilibrium lines, they describe the *compositions* of the liquid and vapor that can simultaneously exist;
- the compositions of the vapor and liquid are not the same;
- in the vapor, the mole fraction of B (the more volatile component of the solution) is greater than that in the liquid;
- in the liquid, the mole fraction of A (the less volatile component) is smaller than that of the vapor.

The vapor in equilibrium with a solution of two or more liquids is **always** richer in the more volatile component.

Temperatures vs. Composition Phase Diagrams (Boiling Point Diagrams)

The lever rule discussed above suggests that if we heat a mixture sufficiently to bring its total vapor pressure into the two-phase region, we will have a means of separating the mixture into two portions which will be enriched in the more volatile and less volatile components respectively. This is the principle on which distillation is based. But what temperature is required to achieve this? Again, we will spare you the mathematical details, but it is possible to construct a plot similar to the Figure 4.5.4 except that the vertical axis represents *temperature* rather than pressure. This kind of plot is called a *boiling point diagram*.

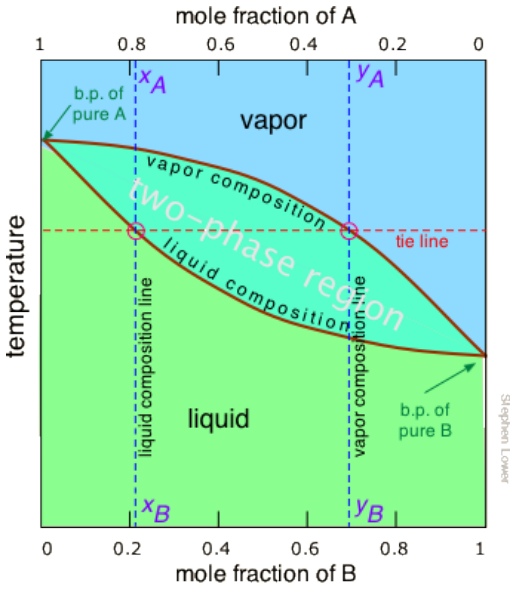


Figure 4.5.4: Boiling point diagram of a volatile two-component system.

Important Properties of Boiling Point Diagrams

Some important things to understand about Figure 4.5.6:

- The shape of the two-phase region is bi-convex, as opposed to the half-convex shape of the pressure-composition plot.
- The slope of the two-phase region is opposite to what we saw in the previous plot, and the areas corresponding to the single-phase regions are reversed. This simply reflects the fact that liquids having a higher vapor pressure boil at lower temperatures, and *vice versa*.
- The horizontal line that defines the temperature is called the *tie line*. Its intercepts with the two equilibrium curves specify the composition of the liquid and vapor in equilibrium with the mixture at the given temperature.
- The vapor composition line is also known as the *dew point line* — the temperature at which condensation begins on cooling.

- The liquid composition line is also called the *bubble point line* — the temperature at which boiling begins on heating.

The tie line shown in Figure 4.5.4 is for one particular temperature. But when we heat a liquid to its boiling point, the composition will change as the more volatile component (B in these examples) is selectively removed as vapor. The remaining liquid will be enriched in the less volatile component, and its boiling point will consequently rise. To understand this process more thoroughly, let us consider the situation at several points during the distillation of an equimolar solution of A and B.

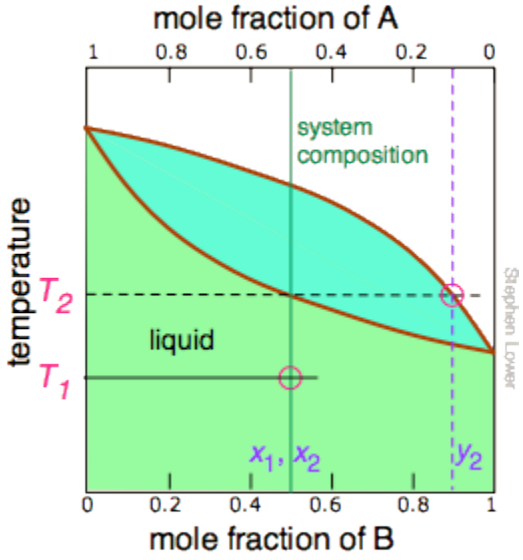


Figure 4.5.5*A*: We begin with the liquid at T_1, below its boiling point. When the temperature rises to T_2, boiling begins and the first vapor (and thus the first drop of condensate) will have the composition y_2.

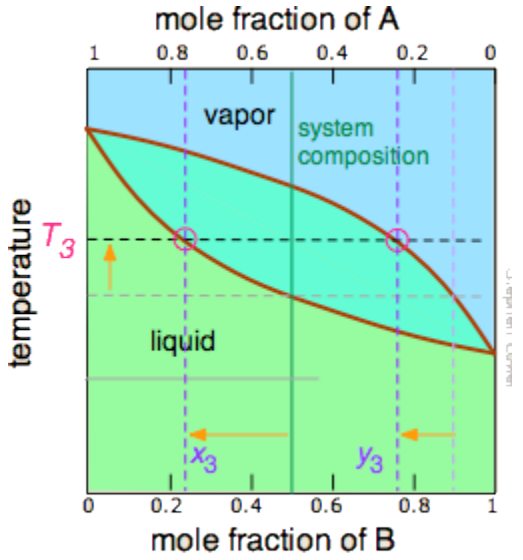


Figure 4.5.5*B*: As the more volatile component B is boiled off, the liquid and vapor/condensate compositions shift to the left (orange arrows).

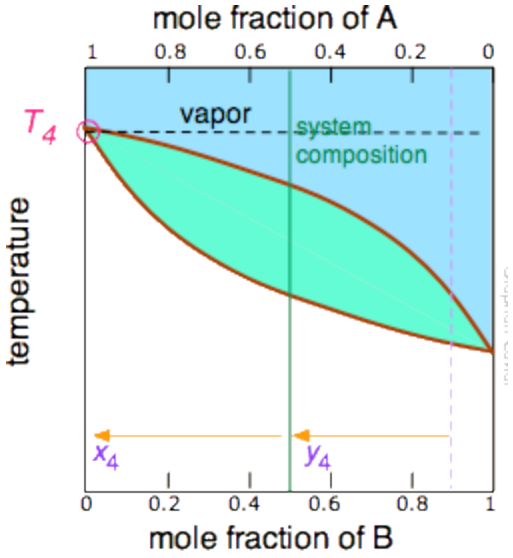


Figure 4.5.5*C*: At T_4, the last trace of liquid disappears. The system is now entirely vapor, of composition y_4.

Notice that the vertical green *system composition* line remains in the same location in the three plots because the "system" is defined as consisting of both the liquid in the "pot" and that in the receiving container which was condensed from the vapor. The principal ideas you should take away from this are that

- distillation can never completely separate two volatile liquids;
- the composition of the vapor and thus of the condensed distillate changes continually as each drop forms, starting at y_2 and ending at y_4 in this example;
- if the liquid is completely boiled away, the composition of the distillate will be the same as that of the original solution.

Laboratory Distillation Setup

The apparatus used for a simple laboratory batch distillation is shown here. The purpose of the thermometer is to follow the progress of the distillation; as a rough rule of thumb, the distillation should be stopped when the temperature rises to about half-way between the boiling points of the two pure liquids, which should be at least 20-30 C° apart (if they are closer, then *fractional distillation*, described below, becomes necessary).

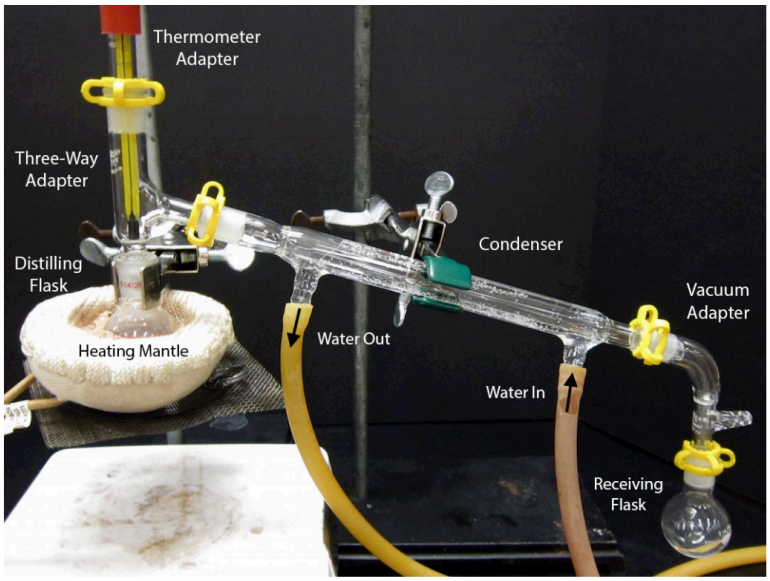


Figure 4.5.6: Simple distillation apparatus. An round-bottom flask is used as a receiving flask. Here the distillation head and fractionating column are combined in one piece. (CC BY-NC-ND; Lisa Nichols (Butte Community College)).

Condensers are available in a number of types. The simple *Liebig condenser* shown above is the cheapest and therefore most commonly used in student laboratories. Several other classic designs increase the surface area separating the vapor/distillate and cooling water, leading to greater heat exchange efficiency and allowing higher throughput.

Fractional Distillation

Although distillation can never achieve complete separation of volatile liquids, it can in principal be carried out in such a way that any desired degree of separation can be achieved if the solution behaves ideally and one is willing to go to the trouble. The general procedure is to distill only a fraction of the liquid, the smaller the better. The condensate, now enriched in the more volatile component, is then collected and re-distilled (again, only a small fraction), thus obtaining a condensate even-more-enriched in the more volatile component. If we repeat this sequence many times, we can eventually obtain almost-pure, if minute, samples of the two components.

However, since this would hardly be practical, there is a better way. To understand it, you need to know about the *lever rule*, which provides a simple way of determining the relative *quantities* (not just the compositions) of two phases in equilibrium. The lever rule is easily derived from **Raoult's** and **Dalton's laws**, but we will simply illustrate it graphically (Figure 4.5.7). The plot shows the boiling point diagram of a simple binary mixture of composition (1). At the temperature corresponding to the tie line, the composition of the liquid corresponds to (2) and that of the vapor to (3).

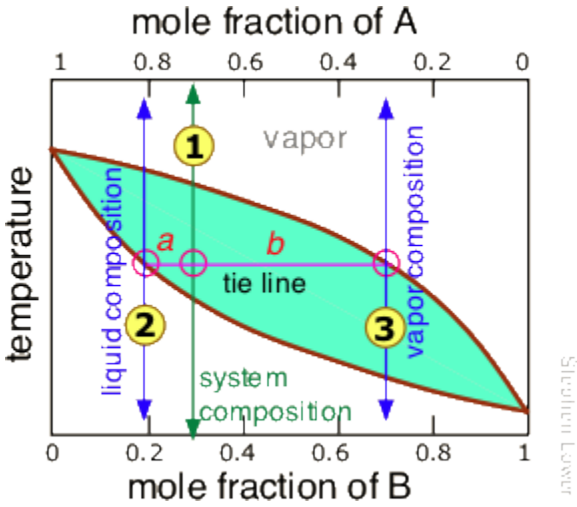


Figure 4.5.7:

So now for the lever rule: the relative quantities of the liquid and the vapor we identified above are given by the lengths of the tie-line segments labeled *a* and *b*. Thus in this particular example, in which *b* is about four times longer than *a*, we can say that the mole ratio of vapor (of composition (3)) to liquid (composition (2)) is 4.

It is not practical to carry out an almost-infinite number of distillation steps to obtain nearly-infinitesimal quantities of the two pure liquids we wish to separate. So instead of collecting each drop of condensate and re-distilling it, we will distil half of the mixture in each step. Suppose you want to separate a liquid mixture composed of 20 mole-% B and 80 mole-% A, with A being the more volatile.

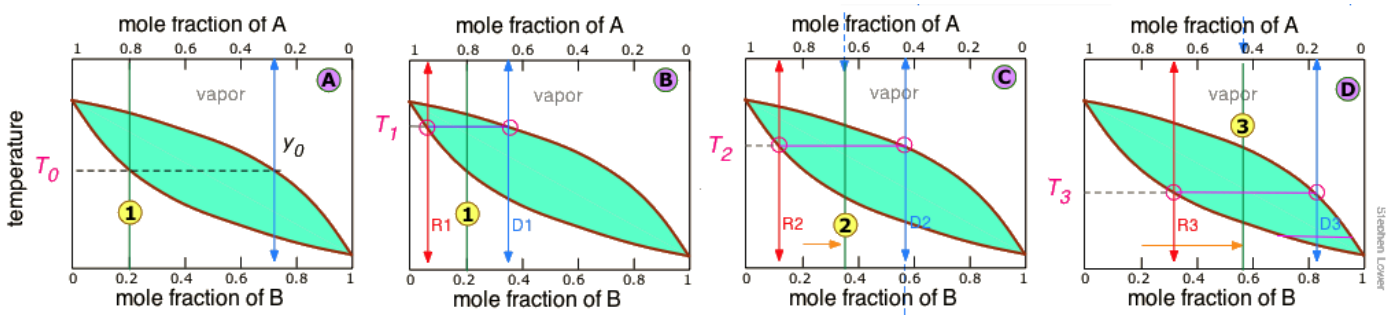


Figure 4.5.8: Steps in Fractional Distillation

A As we heat the mixture whose overall composition is indicated by 1, the first vapor is formed at T_0 and has the composition y_0, found by extending the horizontal dashed line until it meets the vapor curve. This vapor is clearly enriched in B; if it is condensed, the resulting liquid will have a mole fraction x_B approaching that of A in the original liquid. But this is only the first drop, we don't want to stop there!

B As the liquid continues to boil, the boiling temperature rises. When it reaches T_1, we will have boiled away half of the liquid. At this point, the "system" composition (liquid plus vapor) is still the same (1), but is now equally divided between the liquid, which we call "residue" R_1, and the condensed vapor, the *distillate* D_1.

> *How do we know it is equally divided? We have picked T_1 so that the tie line is centered on the system concentration, so by the lever rule, R_1 and D_1 contain equal numbers of moles.*

C We now take the condensed liquid D_1 having the composition 2, and distill half of it, obtaining distillate of composition D_2.

D .. and then carry out yet another distillation, this time using D_3 as our feedstock.

E Our four-stage fractionation has enriched the more volatile solute from 20 to slightly over 80 mole-percent in D_4. The less volatile component A is most concentrated in R_1. R_2 through R_4 are thrown away (but not down the sink, please!)

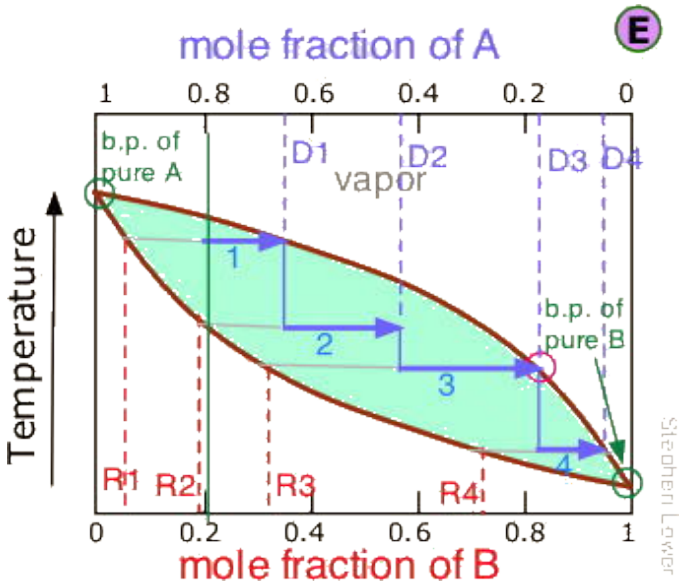


Figure 4.5.9: Boiling point diagrams illustrating four fractional distillation steps.

Azeotropes: the Limits of Distillation (Non-Ideal Behavior)

The boiling point diagrams discussed above apply to solutions that behave in a reasonably ideal manner — that is, to solutions that do not deviate too far from Raoult's law. As we explained above, mixtures of liquids whose intermolecular interactions are widely different do not behave ideally, and may be impossible to separate by ordinary distillation. The reason for this is that under certain conditions, the compositions of the liquid and of the vapor in equilibrium with it become identical, precluding any further separation. These cross-over points appear as "kinks" in the boiling point diagrams (Figure 4.5.10).

Thus in this boiling point diagram for a mixture exhibiting a positive deviation from Raoult's law (Figure 4.5.10*A*), successive fractionations of mixtures correspond to either (1) or (2) bring the distillation closer to the azeotropic composition indicated by the dashed vertical line. Once this point is reached, further distillation simply yields more of the same "high-boiling" azeotrope.

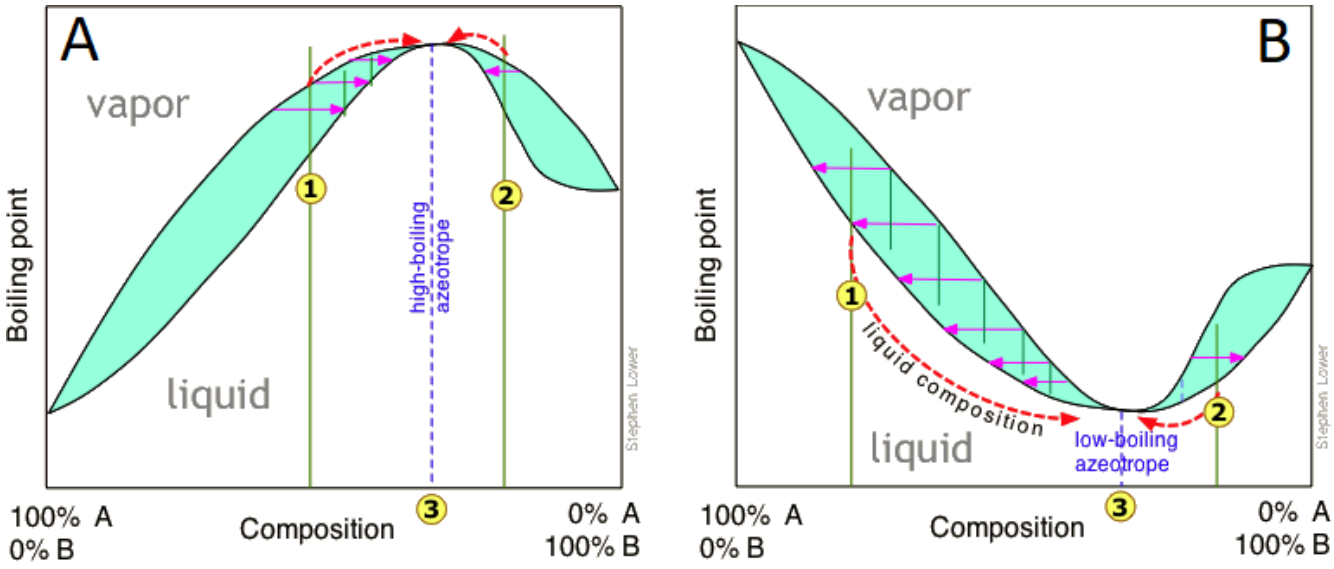


Figure 4.5.10: Maximum Boiling Azeotrope (left) and Maximum Bioling Azeotrope (right).

Distillation of a mixture having a negative deviation from Raoult's law leads to a similar stalemate, in this case yielding a "low-boiling" azeotrope (Figure 4.5.10*B*). High- and low-boiling azeotropes are commonly referred to as *constant-boiling mixtures*, and they are more common than most people think.

Table 4.5.8*: Some constant-boiling mixtures*

Mixture	Azeotrope
Ethanol : water	98%, high, 78.1°C
Hydrochloric acid : water	20.2% high, 108.6°C
Hydrofluoric acid : water	35.6%, 111.3°C
Nitric acid : water	68%, 120.5°C
Sulfuric acid : water	98.3%, 338°C

Distillation of Ethanol

Ethanol is one of the major industrial chemicals, and is of course the essential component of beverages that have been a part of civilization throughout recorded history. Most ethanol is produced by fermentation of the starch present in food grains, or of sugars formed by the enzymatic degradation of cellulose. Because ethanol is toxic to the organisms whose enzymes mediate the fermentation process, the ethanol concentration in the fermented mixture is usually limited to about 15%. The liquid phase of the mixture is then separated and distilled.

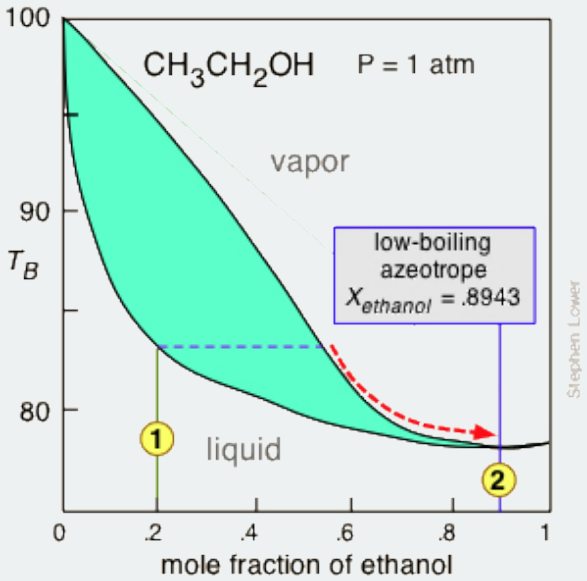


Figure 4.5.11: *The normal boiling point of ethanol is 78.4°C, but its formation of a low-boiling* azeotrope *with water limits the maximum concentration that can be obtained by ordinary distillation to 95.6 volume-% (89.5 mole-%). This concentration is adequate for many applications, for which the product is commonly sold as "95% ethanol".*

For applications requiring anhydrous ethanol ("absolute ethanol "), the most common method is the use of zeolite-based molecular sieves to absorb the remaining water. Addition of benzene can break the azeotrope, and this was the most common production method in earlier years. For certain critical uses where the purest ethanol is required, it is synthesized directly from ethylene.

How to "Break" an Azeotrope

There are four general ways of dealing with azeotropes. The first two of these are known collectively as *azeotropic distillation*.

- **Addition of a third substance** that alters the intermolecular attractions is the most common trick. The drawback is that another procedure is usually needed to remove this other substance.
- **Pressure-swing distillation** takes advantage of the fact that boiling point (*T,X*) diagrams are two-dimensional slices of a (*T,X,P*) diagram in which the pressure is the third variable. This means that the azeotropic composition depends on the pressure, so distillation at some pressure other than 1 atm may allow one to "jump" the azeotrope.
- **Use of a molecular sieve** — a porous material that selectively absorbs one of the liquids, most commonly water when the latter is present at a low concentration.
- **Give up.** It often happens that the azeotropic composition is sufficiently useful that it's not ordinarily worth the trouble of obtaining a more pure product. This accounts for the concentrations of many commercial chemicals such as mineral acids.

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4.6: Colloidal Suspensions

Learning Objectives

- To distinguish between true solutions and solutions with aggregate particles.

Suspensions and colloids are two common types of mixtures whose properties are in many ways intermediate between those of true solutions and heterogeneous mixtures. A suspension is a heterogeneous mixture of particles with diameters of about 1 µm (1000 nm) that are distributed throughout a second phase. Common suspensions include paint, blood, and hot chocolate, which are solid particles in a liquid, and aerosol sprays, which are liquid particles in a gas. If the suspension is allowed to stand, the two phases will separate, which is why paints must be thoroughly stirred or shaken before use. A colloid is also a heterogeneous mixture, but the particles of a colloid are typically smaller than those of a suspension, generally in the range of 2 to about 500 nm in diameter. Colloids include fog and clouds (liquid particles in a gas), milk (solid particles in a liquid), and butter (solid particles in a solid). Other colloids are used industrially as catalysts. Unlike in a suspension, the particles in a colloid do not separate into two phases on standing. The only combination of substances that cannot produce a suspension or a colloid is a mixture of two gases because their particles are so small that they always form true solutions. The properties of suspensions, colloids, and solutions are summarized in Table 4.6.1.

Table 4.6.1: Properties of Liquid Solutions, Colloids, and Suspensions

Type of Mixture	Approximate Size of Particles (nm)	Characteristic Properties	Examples
solution	< 2	not filterable; does not separate on standing; does not scatter visible light	air, white wine, gasoline, salt water
colloid	2–500	scatters visible light; translucent or opaque; not filterable; does not separate on standing	smoke, fog, ink, milk, butter, cheese
suspension	500–1000	cloudy or opaque; filterable; separates on standing	muddy water, hot cocoa, blood, paint

Colloids and Suspensions

Colloids were first characterized in about 1860 by Thomas Graham, who also gave us Graham's law of diffusion and effusion. Although some substances, such as starch, gelatin, and glue, appear to dissolve in water to produce solutions, Graham found that they diffuse very slowly or not at all compared with solutions of substances such as salt and sugar. Graham coined the word colloid (from the Greek kólla, meaning "glue") to describe these substances, as well as the words sol and gel to describe certain types of colloids in which all of the solvent has been absorbed by the solid particles, thus preventing the mixture from flowing readily, as we see in Jell-O. Two other important types of colloids are aerosols, which are dispersions of solid or liquid particles in a gas, and emulsions, which are dispersions of one liquid in another liquid with which it is immiscible.

Colloids share many properties with solutions. For example, the particles in both are invisible without a powerful microscope, do not settle on standing, and pass through most filters. However, the particles in a colloid scatter a beam of visible light, a phenomenon known as the Tyndall effect,The effect is named after its discoverer, John Tyndall, an English physicist (1820–1893). whereas the particles of a solution do not. The Tyndall effect is responsible for the way the beams from automobile headlights are clearly visible from the side on a foggy night but cannot be seen from the side on a clear night. It is also responsible for the colored rays of light seen in many sunsets, where the sun's light is scattered by water droplets and dust particles high in the atmosphere. An example of the Tyndall effect is shown in Figure 4.6.1.



Figure 4.6.1: Tyndall Effect, the Scattering of Light by Colloids (CC BY; LibreTexts)

Although colloids and suspensions can have particles similar in size, the two differ in stability: the particles of a colloid remain dispersed indefinitely unless the temperature or chemical composition of the dispersing medium is changed. The chemical explanation for the stability of colloids depends on whether the colloidal particles are hydrophilic or hydrophobic.

Most proteins, including those responsible for the properties of gelatin and glue, are hydrophilic because their exterior surface is largely covered with polar or charged groups. Starch, a long-branched polymer of glucose molecules, is also hydrophilic. A hydrophilic colloid particle interacts strongly with water, resulting in a shell of tightly bound water molecules that prevents the particles from aggregating when they collide. Heating such a colloid can cause aggregation because the particles collide with greater energy and disrupt the protective shell of solvent. Moreover, heat causes protein structures to unfold, exposing previously buried hydrophobic groups that can now interact with other hydrophobic groups and cause the particles to aggregate and precipitate from solution. When an egg is boiled, for example, the egg white, which is primarily a colloidal suspension of a protein called albumin, unfolds and exposes its hydrophobic groups, which aggregate and cause the albumin to precipitate as a white solid.

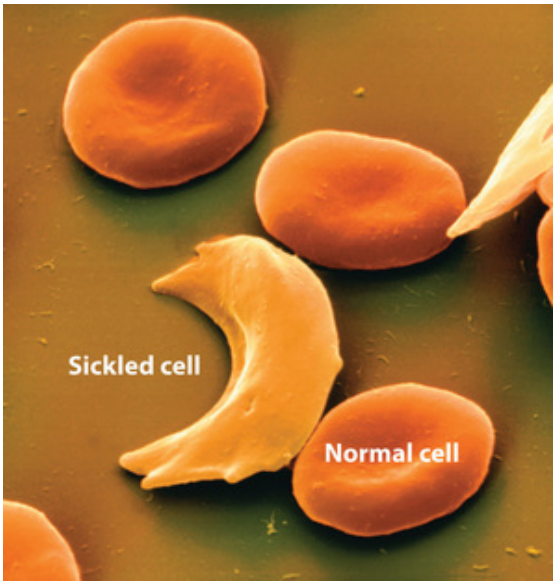


Figure 4.6.2: Sickle-Cell Anemia The characteristic shape of sickled red blood cells is the result of fibrous aggregation of hemoglobin molecules inside the cell.

A normal blood cell is circular in shape with a dimple in the middle, a sickled cell is banana shaped.

In some cases, a stable colloid can be transformed to an aggregated suspension by a minor chemical modification. Consider, for example, the behavior of hemoglobin, a major component of red blood cells. Hemoglobin molecules normally form a colloidal suspension inside red blood cells, which typically have a “donut” shape and are easily deformed, allowing them to squeeze through the capillaries to deliver oxygen to tissues. In a common inherited disease called sickle-cell anemia, one of the amino acids in hemoglobin that has a hydrophilic carboxylic acid side chain (glutamate) is replaced by another amino acid that has a hydrophobic side chain (valine). Under some conditions, the abnormal hemoglobin molecules can aggregate to form long, rigid fibers that cause the red blood cells to deform, adopting a characteristic sickle shape that prevents them from passing through the capillaries (Figure 4.6.2). The reduction in blood flow results in severe cramps, swollen joints, and liver damage. Until recently, many patients with sickle-cell anemia died before the age of 30 from infection, blood clots, or heart or kidney failure, although individuals with the sickle-cell genetic trait are more resistant to malaria than are those with “normal” hemoglobin.

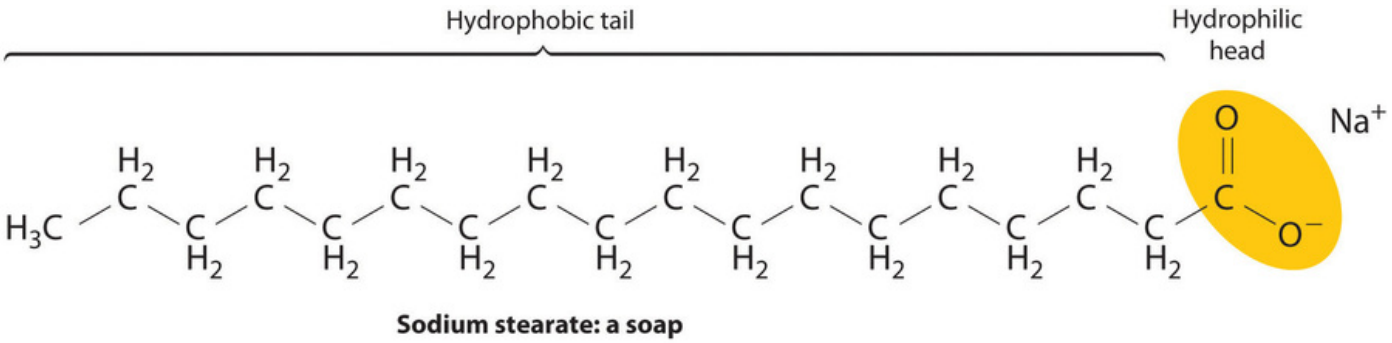


Figure 4.6.3: Formation of New Land by the Destabilization of a Colloid Suspension. This satellite photograph shows the Mississippi River delta from New Orleans (top) to the Gulf of Mexico (bottom). Where seawater mixes with freshwater from the Mississippi River, colloidal clay particles in the river water precipitate (tan area).

Aggregation and precipitation can also result when the outer, charged layer of a particle is neutralized by ions with the opposite charge. In inland waterways, clay particles, which have a charged surface, form a colloidal suspension. High salt concentrations in seawater neutralize the charge on the particles, causing them to precipitate and form land at the mouths of large rivers, as seen in the satellite view in Figure 4.6.3. Charge neutralization is also an important strategy for precipitating solid particles from gaseous colloids such as smoke, and it is widely used to reduce particulate emissions from power plants that burn fossil fuels.

Emulsions

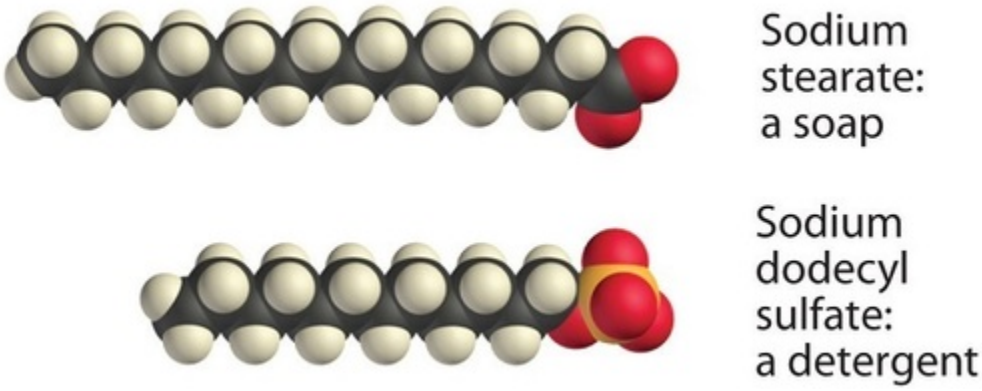
Emulsions are colloids formed by the dispersion of a hydrophobic liquid in water, thereby bringing two mutually insoluble liquids, such as oil and water, in close contact. Various agents have been developed to stabilize emulsions, the most successful being molecules that combine a relatively long hydrophobic “tail” with a hydrophilic “head”:



Sodium stearate: a soap

Bond line drawing of soap, The hydrophobic tail is a long hydrocarbon chain. The hydrophilic heat is a carbon double bonded to an oxygen and single bonded to a negatively charged oxygen.

Examples of such emulsifying agents include soaps, which are salts of long-chain carboxylic acids, such as sodium stearate $[CH_3(CH_2)_{16}CO_2{-}Na^+]$, and detergents, such as sodium dodecyl sulfate $[CH_3(CH_2)_{11}OSO_3{-}Na^+]$, whose structures are as follows:



When you wash your laundry, the hydrophobic tails of soaps and detergents interact with hydrophobic particles of dirt or grease through dispersion forces, dissolving in the interior of the hydrophobic particle. The hydrophilic group is then exposed at the surface of the particle, which enables it to interact with water through ion–dipole forces and hydrogen bonding. This causes the particles of dirt or grease to disperse in the wash water and allows them to be removed by rinsing. Similar agents are used in the food industry to stabilize emulsions such as mayonnaise.

A related mechanism allows us to absorb and digest the fats in buttered popcorn and French fries. To solubilize the fats so that they can be absorbed, the gall bladder secretes a fluid called bile into the small intestine. Bile contains a variety of bile salts, detergent-like molecules that emulsify the fats.

Micelles

Detergents and soaps are surprisingly soluble in water in spite of their hydrophobic tails. The reason for their solubility is that they do not, in fact, form simple solutions. Instead, above a certain concentration they spontaneously form micelles, which are spherical or cylindrical aggregates that minimize contact between the hydrophobic tails and water. In a micelle, only the hydrophilic heads are in direct contact with water, and the hydrophobic tails are in the interior of the aggregate (Figure $4.6.4a$).

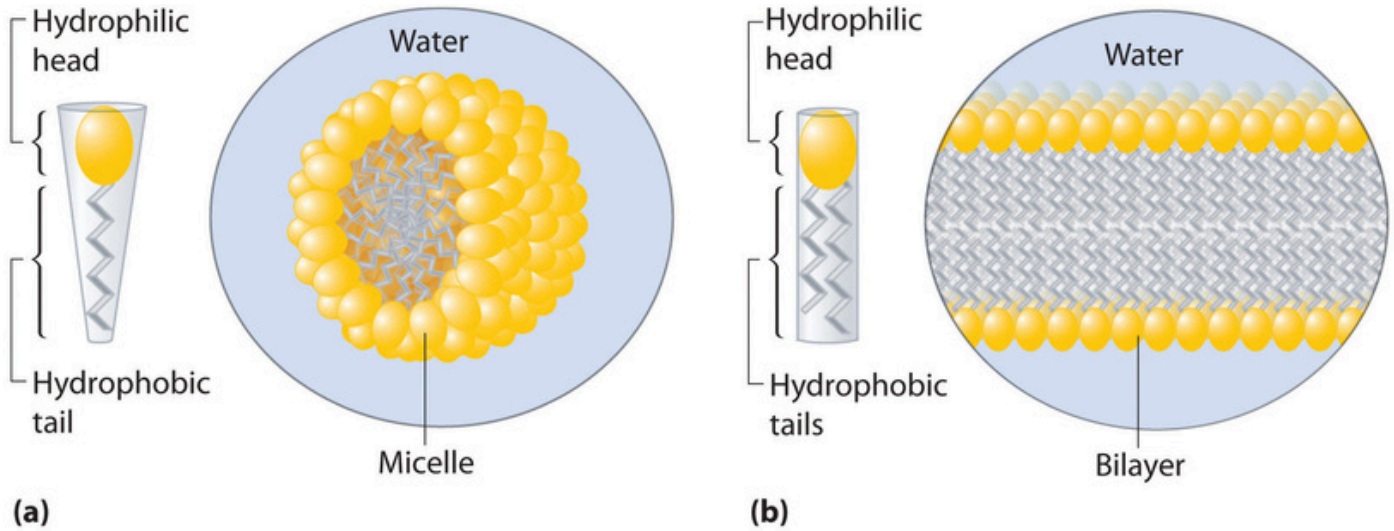
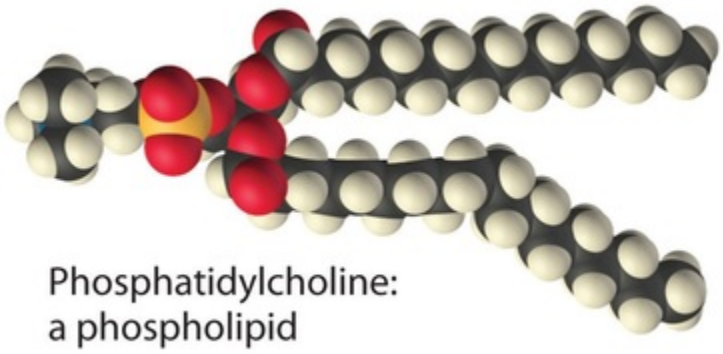


Figure 4.6.4: Micelles and a Phospholipid Bilayer. (a) Soaps and detergents, which contain a single hydrophobic tail on each molecule, form spherical micelles with the intertwined tails in the interior and the hydrophilic head groups on the exterior. (b) Phospholipids, which have two hydrophobic tails, tend to form extended double layers in which the hydrophobic tails are sandwiched between the hydrophilic head groups.

A large class of biological molecules called phospholipids consists of detergent-like molecules with a hydrophilic head and two hydrophobic tails, as can be seen in the molecule of phosphatidylcholine. The additional tail results in a cylindrical shape that prevents phospholipids from forming a spherical micelle. Consequently, phospholipids form bilayers, extended sheets consisting of a double layer of molecules. As shown in Figure 4.6.4*b*, the hydrophobic tails are in the center of the bilayer, where they are not in contact with water, and the hydrophilic heads are on the two surfaces, in contact with the surrounding aqueous solution.



A cell membrane is essentially a mixture of phospholipids that form a phospholipid bilayer. One definition of a cell is a collection of molecules surrounded by a phospholipid bilayer that is capable of reproducing itself. The simplest cells are bacteria, which consist of only a single compartment surrounded by a single membrane. Animal and plant cells are much more complex, however, and contain many different kinds of compartments, each surrounded by a membrane and able to carry out specialized tasks.

Summary

A suspension is a heterogeneous mixture of particles of one substance distributed throughout a second phase; the dispersed particles separate from the dispersing phase on standing. In contrast, the particles in a colloid are smaller and do not separate on standing. A colloid can be classified as a sol, a dispersion of solid particles in a liquid or solid; a gel, a semisolid sol in which all of the liquid phase has been absorbed by the solid particles; an aerosol, a dispersion of solid or liquid particles in a gas; or an emulsion, a dispersion of one liquid phase in another. A colloid can be distinguished from a true solution by its ability to scatter a beam of light, known as the Tyndall effect. Hydrophilic colloids contain an outer shell of groups that interact favorably with water, whereas hydrophobic colloids have an outer surface with little affinity for water. Emulsions are prepared by dispersing a hydrophobic liquid in water. In the absence of a dispersed hydrophobic liquid phase, solutions of detergents in water form organized spherical aggregates called micelles. Phospholipids are a class of detergent-like molecules that have two hydrophobic

tails attached to a hydrophilic head. A bilayer is a two-dimensional sheet consisting of a double layer of phospholipid molecules arranged tail to tail with a hydrophobic interior and a hydrophilic exterior. Cells are collections of molecules that are surrounded by a phospholipid bilayer called a cell membrane and are able to reproduce themselves.

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4.E: Solutions (Exercises)

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

Q.1

A student goes to the hospital and has blood work done and the results state that he has a bromide count of $3.17 \frac{mg}{dL}$.

a. What is the molar concentration of the students blood?
b. What is the molality of the student's blood if the density of his blood was found to be $1.06 \frac{g}{mL}$?
c. How much of the students blood would be require to get $3g$ of bromide?

Solution

The molar mass of bromide is $79.90 \frac{g}{mol}$. $1L = 10dL$, $1g = 1000mg$

$$\left(\frac{3.17\ \cancel{mg}}{1\ \cancel{dL}}\right)\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{10\ \cancel{dL}}{1\text{L}}\right)\left(\frac{1\text{mol}}{79.90\ \cancel{g}}\right) = 3.97 \times 10^{-4}\ \frac{mol}{L}$$

Assume there is 1L of solution. Modality (m) is calculated by:

$$3.17 \text{ x } 10^{-2}\ \cancel{g}\left(\frac{1 \text{ mol}}{79.90\ \cancel{g}}\right)\left(\frac{1}{1.06 \text{ kg}}\right) = 3.74 \times 10^{-4} \frac{mol}{kg}$$

If we know that there is $3.17 \times 10^{-2} g$ of bromide in $1L$ of blood, so all that needs to be done is divide $3g$ by $3.17 \times 10^{-2}\ \frac{g}{L}$:
Volume of Blood = 94.64 L

Q.5

Given a 3.1416 M aqueous solution of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ with a density of $1.5986\ \frac{\text{g}}{\text{mL}}$. Calculate the molality of this solution, remember that the molar mass of sucrose is $342.297 \frac{\text{g}}{\text{mol}}$.

Solution

Before we calculate the molality of this solution, don't forget that molarity is just mol/L so we will multiply the molarity of the solution by 1 L to isolate the moles.

$$1.00\ \cancel{L}\ \text{Water} = \frac{3.1416\ mol\ \text{Sucrose}}{1.00\ \cancel{L}\ \text{Water}} = 3.1416\ mol\ \text{Sucrose}$$

Once we have the moles of Sucrose we will multiply it by the molar mass of sucrose in order to find the number of sucrose grams present in the solution:

$$3.1416\ \cancel{mol}\ \text{Sucrose} = \frac{342.297\ g\ \text{Sucrose}}{1.00\ \cancel{mol}\ \text{Sucrose}} = 1075.4\ g\ \text{Sucrose}$$

We next will multiply the density by 1000 mL so as get the number of grams per liter, this way we can find the total grams of the solution and can subtract the sucrose grams from the solution grams to find the grams of water.

$$1000\ \cancel{mL}\ = \frac{1.5986\ g\ \text{SucroseSoln}}{1.00\ \cancel{mL}\ \text{SucroseSoln}} = 1598.6\ g/L\ \text{SucroseSoln}$$

$$\text{Water grams} = [1598.6g\ \text{Sucrose Soln.}] - [1075.4g\ \text{Sucrose}] = 523.2g\ \text{Water}\ = 0.5232\ kg\ \text{Water}$$

Lastly we divide the moles of Sucrose by the kg of water in order to get molality.

$$\frac{3.1416\ mol\ \text{Sucrose}}{0.5232\ kg\ \text{Water}} = 6.005\ molal$$

Q.9

A solution contains 75% of ethanol (C_2H_6O) by mass and the rest is water.

a. What is the density of the solution if there is 15 mol of ethanol per liter of solution?
b. To prepare a 3.5L of 2M ethanol, how many milliliters of the solution is needed?

Solution

a) For easy calculation, assume that there is 1 L of the solution. Using:

$$\text{mol} = \text{molarity} \times \text{volume} \tag{4.E.1545}$$

The mol of 15M ethanol in 1L is 15 mol. The molar mass of ethanol is $46.068\frac{g}{mol}$. Using the equation below:

$$\text{ethanol mol} = \frac{\text{mass ethanol}}{\text{ethanol molar mass}} \tag{4.E.1546}$$

$$\text{ethanol mass in the solution} = \text{ethanol mol} \times \text{molar mass} = (15mol)(46.068\frac{g}{mol}) = 691.02g \tag{4.E.1547}$$

Ethanol is 75% of the solution by mass, therefore:

$$\text{mass of solution} \times 0.75 = \text{mass of ethanol} \tag{4.E.1548}$$

$$\text{mass of solution} \times 0.75 = 691.02g \tag{4.E.1549}$$

$$\text{mass of solution} = \frac{691.02g}{0.75} = 921.36g \tag{4.E.1550}$$

The equation to calculate density is:

$$\text{Density} = \frac{\text{mass}}{\text{volume}} \tag{4.E.1551}$$

$$\text{Density} = \frac{921.36g}{1L} = 0.921\frac{g}{ml} \tag{4.E.1552}$$

b)To prepare a 3.5L of 2M ethanol;

$$\text{ethanol mol needed} = \text{molarity} \times \text{volume} = (2\,\text{M})(3.5\,\text{L}) = 7\,\text{mol} \tag{4.E.1553}$$

$$V_{\text{ethanol needed}} = \frac{\text{mol needed}}{\text{molarity}} = \frac{7\,\text{mol}}{15\,\text{mol}} \times 1\,\text{L} = 0.467\,\text{L} \tag{4.E.1554}$$

0.467L of the solution is needed, which is 467mL.

Q.14

Rewrite the following balanced equations as net ionic equations.

a. $H_2SO_4\,(aq) + 2\,NaOH\,(aq) \rightarrow 2\,H_2O\,(l) + Na_2SO_4\,(aq)$
b. $2\,Na_3PO_4\,(aq) + 3\,CaCl_2\,(aq) \rightarrow 6\,NaCl\,(aq) + Ca_3(PO_4)_2\,(s)$
c. $BaCl_2\,(aq) + Na_2SO_4\,(aq) \rightarrow BaSO_4\,(s) + 2\,NaCl\,(aq)$
d. $2\,AgNO_3\,(aq) + ZnCl_2\,(aq) \rightarrow 2\,AgCl\,(s) + Zn(NO_3)_2\,(aq)$

Solution

a. $2\,H^+\,(aq) + 2\,OH^-\,(aq) \longrightarrow 2\,H_2\,O\,(l)$
b. $2\,PO_4{}^{3-}\,(aq) + 3\,Ca^{2+}\,(aq) \longrightarrow Ca_3(PO_4)_2\,(s)$
c. $Ba^{2+}\,(aq) + SO_4{}^{2-}\,(aq) \longrightarrow BaSO_4\,(s)$
d. $2\,Ag^{2+}\,(aq) + Cl^-\,(aq) \longrightarrow 2\,AgCl\,(s)$

Q.15

Write the balanced chemical equation for the titration of H_2SO_4 with KOH, then find the volume of a 5.49 M KOH solution needed to neutralize 36.2 g of H_2SO_4 .

Solution

The balanced equation of H_2SO_4 with KOH is:

$$H_2SO_4\,(aq) + 2\,KOH\,(aq) \longrightarrow K_2SO_4\,(aq) + 2\,H_2O\,(l)$$

Calculate the amount of moles of H_2SO_4 being neutralized:

$$n_{H_2SO_4} = 36.2\text{ g } H_2SO_4 \times \frac{1\text{ mol } H_2SO_4}{98.079\text{ g } H_2SO_4} = 0.369\text{ mol } H_2SO_4$$

Using stoichiometry to find the amount of moles of KOH needed to neutralize the amount of H_2SO_4 present:

$$n_{KOH} = 0.369\text{ mol } H_2SO_4 \times \frac{2\text{ mol KOH}}{1\text{ mol } H_2SO_4} = 0.738\text{ mol KOH}$$

Calculate the volume of the 5.49 M KOH solution needed to neutralize the amount of H_2SO_4 present:

$$V_{KOH} = 0.738\text{ mol KOH} \times \frac{1\text{ L}}{5.49\text{ mol KOH}} = 0.134\text{ L} = 134\text{ mL}$$

Therefore, approximately 134 mL of the 5.49 M KOH solution is needed to neutralize 36.2 g H_2SO_4.

Q.16

Phosphoric acid is made industrially as a by-product of the extraction of calcium phosphate

$$Ca_3(PO_4)_2 + 6\,HNO_3 + 12\,H_2O \longrightarrow 2\,H_3PO_4 + 3\,Ca(NO_3)_2 + 12\,H_2O$$

What volume of 8.5 M phosphoric acid is generated by the reaction of 4.5 metric tons (4500 kg) of calcium phosphate?

Solution

$$4500\,kg\ Ca_3(PO_4)_2 \times \left(\frac{1000\,g}{1\ kg}\right) \times \left(\frac{1\text{ mol}}{310\text{ g}}\right) \times \left(\frac{2\,H_3PO_4}{1\,Ca_3(PO_4)_2}\right) \times \left(\frac{1\text{ L}}{8.5\text{ moles}}\right) = 3415.56\,L\ H_3PO_4$$

Q.19

Write a balanced equation for the acid-base reaction that leads to the production of each of the following salts.

a. $BaSO_4$
b. $MgSO_3$
c. $PbSO_4$
d. $AgCl$

Solution

a. $Ba(OH)_2\,(aq) + H_2SO_4\,(aq) \rightleftharpoons BaSO_4\,(s) + 2\,H_2O\,(l)$
b. $Mg(OH)_2\,(s) + H_2SO_3\,(aq) \rightleftharpoons MgSO_3\,(s) + 2\,H_2O\,(l)$

c. $\mathrm{Pb(OH)_2\,(s) + H_2SO_4\,(aq) \rightleftharpoons PbSO_4\,(s) + 2\,H_2O\,(l)}$
d. $\mathrm{AgOH\,(s) + HCl\,(aq) \rightleftharpoons AgCl\,(s) + H_2O\,(l)}$

Q.21

Hydrogen selenide is classified as a binary acid that has similar properties as hydrogen sulfide. Write down the balanced equation of hydrogen selenide reacting with the base potassium hydroxide and name the salt product of the reaction.

Solution

When the acid $\mathrm{H_2S}$ reacts with the base KOH, the reaction goes as follows:

$$\mathrm{H_2S + 2\,KOH \longrightarrow K_2S + 2\,H_2O}$$

Forming potassium sulfide.

Similarly, since $\mathrm{H_2Se}$ has similar properties as $\mathrm{H_2S}$, a similar reaction occurs:

$$\mathrm{H_2Se + 2\,KOH \longrightarrow K_2Se + 2\,H_2O}$$

Potassium selenide is the salt product of the reaction.

Q.25

A student working with an unknown solution of hydrochloric acid is assigned the task of finding its concentration. The student places a 200.0 mL sample of the solution in a 350.0 mL Erlenmeyer flask and titrates the solution with a 0.1234 M solution of sodium hydroxide, where a phenolphthalein indicator is used to find the endpoint. The endpoint is found to be 31.416 mL, what is the concentration of the original hydrochloric acid solution sample?

Solution

Remember that in titration of a strong acid and base, when the endpoint is reached the number of moles used is equal, so the number of moles of NaOH at the endpoint are equal to that of HCl. Use this information to find moles of NaOH from the concentration and volume used to titrate.

$$\mathrm{Concentration\ of\ X} = \frac{\mathrm{moles\ of\ X}}{\mathrm{liters\ of\ X}}$$

Use dimensional analysis to convert concentration of NaOH to moles using the known amount of volume titrated, in liters:

$$0.031416\ \cancel{\mathrm{liter}}\ \mathrm{NaOH} = \frac{0.1234\ \mathrm{mol\,NaOH}}{1.00\ \cancel{\mathrm{liter}}\ \mathrm{Na\text{-}OH}} = 0.003877\ \mathrm{mol}$$

Now because we know that the moles of NaOH are equal to the moles of HCl we simply plug in our calculated moles and known original sample volume, in liters, to find the concentration of HCl:

$$\mathrm{Concentration\ of\ HCl} = \frac{0.003877\ \mathrm{mol\ HCl}}{0.200\ \mathrm{liters\ HCl}} = 0.019385\ \mathrm{M\ HCl}$$

The concentration of the original hydrochloric acid solution sample was, therefore, 0.019385 M.

Q.41

The vapor pressure of salicylic acid $\mathrm{C_7H_6O_3}$ at 200°C is 0.1598 atm. A 19.0 g sample of ethanol $\mathrm{C_2H_6O}$ is dissolved in 60.0 g of salicylic acid. Calculate the vapor pressure of salicylic acid above the resulting solution.

Solution

First find the molar masses of salicylic acid and ethanol. Then use them to compute the chemical amounts of the two in solution.

$$n_{C_2H_6O} = 19.0\ g\ C_2H_6O \times \frac{1\ mol\ C_2H_6O}{46.068\ g\ C_2H_6O} = 0.4124\ mol\ {}_2CH_6O$$

$$n_{C_7H_6O_3} = 60.0\ g\ C_7H_6O_3 \times \frac{1\ mol\ C_7H_6O_3}{138.121\ g\ C_7H_6O_3} = 0.4344\ mol\ {}_7CH_6O_3$$

The mole fraction of ethanol in the solution equals

$$X_{C_2H_6O} = \frac{0.4124}{0.4344 + 0.4124} = 0.4870$$

The change in vapor pressure of the salicylic acid due to the presence of of the ethanol is

$$\Delta P_{C_4H_6O_3} = -X_{C_4H_6O_3} \times P^{\circ}_{C_4H_6O_3} = -0.5130 \times 0.1518\ atm = -0.08198$$

The final vapor pressure of the salicylic acid equals its original vapor pressure P° plus the change. This is 0.1598 atm minus 0.08198 atm, which is 0.07782 atm.

Q.43

When 53 mol of an unknown compound was added to 100 g of water, the normal boiling point of water increased to 101.1°C. What is the boiling point elevation constant of water? The compound does not dissociate in solution.

Solution

The relevant relationship here is the colligative property associated with boiling point elevation

$$\Delta T_b = iK_bm \tag{4.E.1555}$$

$$\Delta T_b = 101.1^o\,C - 100^o\,C = 1.1^o\,C \tag{4.E.1556}$$

Since the compound was told to not dissociation, we know that the van't Hoff factors is 1:

$$i = 1 \tag{4.E.1557}$$

$$m = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{53\,mol}{0.100\,kg} = 0.53\frac{mol}{g} \tag{4.E.1558}$$

$$1.1^oC = (1) \times K_b \times (0.53\frac{mol}{g}) \tag{4.E.1559}$$

$$K_b = \frac{1.1^oC}{0.53\frac{mol}{kg}} = 2.075\frac{^oC\ kg}{mol} \tag{4.E.1560}$$

This problem does not give the correct constant though 0.513:

https://chem.libretexts.org/Referenc...perties/B5%3A_Ebullioscopic_(Boiling_Point_Elevation)_Constants

Q.45

When 5.82 g of uniformly dissociating unknown salt, YX, is dissolved in 100.0 g of water, the boiling point of the water is raised by 0.20°C. When 7.09 g of uniformly dissociating unknown salt, ZX, is dissolved in 200.0 g of water, the boiling point of the water is raised by 0.30°C. Assuming both have a van't hoff factor of 2, identify the elements that X, Y, and Z represent.

Solution

For both salts, one can utilize the boiling point elevation expression (including the van't hoff factor):

$$\Delta T = i \times K_b \times m$$

and by substituting moles solute over mass solvent into the molality, m, one can derive that:

$$n_{\text{salt}} = \frac{\Delta T \times m_{\text{water}}}{i \times K_b}$$

From this we get the moles of each salt present, and can therefore get their molar mass by dividing their mass by moles present. Next, subtracting the heavier salt by the lighter salt will yield the molar mass of X, $\sim 35.5 \frac{\text{g}}{\text{mol}}$. Subtracting this from the molar masses of each salt will then yield Y and Z respectively.

$\Delta T = i \times m \times K_b = 2 \times m \times 0.512 = 0.2,\ \text{m of YX} = 0.1953 \frac{\text{mol}}{\text{kg}};\ m \times 0.1kg = 0.0195 \text{ mol};\ \frac{5.82}{0.0195} = 298.46\ \frac{\text{g}}{\text{mol}}$

$\Delta T = i \times m \times K_b = 2 \times m \times 0.512 = 0.3,\ m\ of\ \text{ZX} = 0.2930 \frac{\text{mol}}{\text{kg}};\ m \times 0.2kg = 0.0586 \text{ mol};\ \frac{7.09}{0.0586} = 120.99 \frac{\text{g}}{\text{mol}}$

molar mass difference between Y and Z = $298.46 - 120.99 = 177.47 \frac{\text{g}}{\text{mol}}$

Q.47

Camphor is a useful agent for determining solute's molar mass. Camphor's melting point and K_f are given at 451.55 K and $37.7 \frac{\text{K kg}}{\text{mol}}$. Find the freezing point of the solution of 0.72 g of glucose is dissolved in the 30.0 g of camphor.

Solution

Since we are evaluating glucose as the solute, $i = 1$.

$$\Delta T = -iK_f m \tag{4.E.1561}$$

First find number of moles of glucose in the solution using molar mass.

$$\text{Moles}_{\text{glucose}} = \frac{(0.72g)}{(180.1559 \frac{g}{mol})} = 0.0040mol \tag{4.E.1562}$$

Molality then can be determined.

$$m = \frac{(0.0040mol)}{(0.030kg)} = 0.13 \frac{mol}{kg} \tag{4.E.1563}$$

Freezing then can be easily found as such:

$$\Delta T = -iK_f m = -(1)(37.7 \frac{^oC\ kg}{mol})(0.13 \frac{mol}{kg}) = -4.9^oC \tag{4.E.1564}$$

The freezing is $451.55K - 4.9K = 446.65K = 173.5^oC$.

Q.48

It is observed that 2 grams of a non-electrolyte solute dissolved in 100 grams of benzene lowered the freezing point of the solution by 0.40°C compared to pure benzene. Given that the freezing point depression constant of benzene is 5.12 K kg/mol, find the molar mass of the solute. If it is given that the molecular formula of the solute is X_8 where X is an element, what is the formula of the solute?

Solution

$$\Delta T = -ik_f m$$

It is given that

$$\Delta T = 0.40°C \tag{4.E.1565}$$

Since the solution is a non-electrolyte, i=1

Hence,

$$\frac{0.40}{K_f} = m$$

$$m = \frac{\frac{2}{\text{Molecular Mass}}}{100 \times 10^{-3}} = \frac{\frac{2}{\text{Molecular Mass}}}{0.1}$$

Hence, we get

$$\frac{0.40 \times 0.1}{K_f} = \frac{2}{\text{Molecular Mass}}$$

$$\text{Molecular Mass } = \frac{2K_f}{0.40 \times 0.1}$$

Hence, the Molecular Mass of the solute is $256\ \frac{g}{mol}$

Since the Molecular Mass of the solute is $256\ \frac{g}{mol}$, we can say that,

$$\text{Molecular Mass of X} = \frac{256}{8} = 32$$

The solute is S_8.

Q.49

At what temperature does the first ice crystals begin to form in a 27% salt (by mass) aqueous solution of NaCl? As the crystallization of water carries on, the remaining solution becomes more concentrated, so what happens to the freezing point of the solution? Given that the freezing point depression constant (K_f) of water is $1.86\frac{^oC\ kg}{mol}$.

Solution

$$27\%\ \text{NaCl(aq)} = \frac{27\ g\ \text{NaCl}}{73\ g\ \text{H}_2\text{O}} \tag{4.E.1566}$$

$$molality = \frac{27\ g\ \text{NaCl}}{73\ g\ \text{H}_2\text{O}} \times \frac{mol\ \text{NaCl}}{58.44\ g} \times \frac{1000\ g}{1\ kg} = 6.33\ m \tag{4.E.1567}$$

$$\Delta T = -i \times m \times K_p = -2 \times 6.33\frac{mol}{kg} \times 1.86\frac{^oC \cdot kg}{mol} = -23.5^oC \tag{4.E.1568}$$

The first ice crystal begins to appear at -23.5^oC, as the solution becomes more concentrated, its freezing point decreases further because freezing point depression is a colligative property, so the freezing point of a solution is lower than that of the pure solvent and is directly proportional to the molality of the solute.

Q.50

When homemade ice cream is being made, the temperature ranging downward from -3°C are needed. Ice cubes from a freezer have a temperature of about -12°C, which is cold enough; however, when the ice cream mixture is mixed with the ice cubes, the liquid balances out to 0°C, which is too warm. To obtain a liquid that is cold enough, salt NaCl is dissolved in water and ice is added to the saltwater. The salt lowers the freezing point of the water enough so that it can freeze the liquid inside the ice cream maker. The instruction for the ice cream maker say to add one part salt to 11 parts water (by mass). What is the freezing point of this solution in °C? Assume the NaCl dissociates fully into ions, and that the solution is ideal.

Solution

$$\Delta T_f = -ik_f m \tag{4.E.1569}$$

$$\frac{1.00\ g\ \text{NaCl}}{53.5\frac{g}{mol}} = 0.01869\ mol\ \text{NaCl} \tag{4.E.1570}$$

$$m = \frac{0.01869\ mol}{11.00g(\frac{1\ kg}{1000\ g})} = 1.699m \tag{4.E.1571}$$

$$x - (-12°C) = -(2) \times (1.86\frac{°C}{m}) \times (1.699m) \tag{4.E.1572}$$

$$x = -18.32°C \tag{4.E.1573}$$

Q.53

A sample of a purified unknown compound is dissolved in toluene, diluting the solvent to a volume of 1.05 mL. The resulting solution has an osmotic pressure of 0.025 atm at 275 K. If the solute has a molar mass of 46.06 g/mol, how many grams of the unknown compound were added?

Solution

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

and we know $T = 275K$, $R = 0.0821\frac{L\ atm}{mol\ K}$ and Π=0.025 atm

Thus V= 1.05 mL

Since we need V in liters because the units of R are $\frac{L\ atm}{mol\ K}$, we use unit conversions:

$$1.05\ mL \times \frac{1L}{1000mL} = 0.00105\ L$$

Plug in the values we know to find n

$$0.025 = \frac{n \times 0.0821 \times 275}{0.00105}$$

$$\frac{0.025 \times 0.00105}{0.0821 \times 275} = n$$

$$n = 1.163 \times 10^{-6}$$

Now that we know number of moles we just have to multiply the number of moles by the molar mass to find grams of substance.

$$(1.163 \times 10^{-6}) \times 46.06844\frac{g}{mol} = 5.356 \times 10^{-5}g$$

Q.57

An amount of hydrogen gas (H_2) with a partial pressure of 4.6 atm is dissolved in water and this solution is sealed. The Henry's Law constant K for this solution at $25°C$ is $7.8 \times 10^{-4}\frac{\text{M}}{\text{atm}}$.

a. How many moles of hydrogen gas will dissolve per liter of water? Assume the density of water is $1.0\frac{\text{grams}}{\text{cm}^3}$ and has not been affected by the temperature.
b. What will the dissolved gas molecules do if the sealed solution is unsealed?

Solution

a) According to Henry's Law,

$$C = k \times P_{\text{gas}}$$

In this equation, C = concentration of gas (M), k = Henry's Law constant ($\frac{M}{atm}$), and P_{gas} = partial pressure of gas.

So, given k and P_{gas}:

$$C = 7.8 \times 10^{-4} \frac{M}{atm} \times 4.6\ atm$$

$$C = 0.003588 \frac{mol\ \text{H}_2}{L_{\text{water}}}$$

b) The partial pressure of H_2 in the Earth's atmosphere is less than 1 atm. When the solution is unsealed, the H_2 molecules will no longer be under enough pressure to dissolve in water, so they will quickly bubble out of the solution and escape as gas into the surroundings.

Q.59

Propene is a colorless organic compound with a weak but unpleasant smell. However, a company can take advantage of its chemical properties to produce propanol:

$$\text{C}_3\text{H}_6 + \text{H}_2\text{O} \longrightarrow \text{CH}_3(\text{CH}_2)_2\text{OH}$$

- The heat of formation of propene is $20.4 \frac{\text{kJ}}{\text{mol}}$.
- The heat of formation of H_2O is $-241.8 \frac{\text{kJ}}{\text{mol}}$.
- The heat of formation of $\text{CH}_3(\text{CH}_2)_2\text{OH}$ is $-104.6 \frac{\text{kJ}}{\text{mol}}$.

What suggestions can you give to the company regarding the conditions of pressure and temperature that will have a maximum yield of propanol at equilibrium without calculating the actual data?

Solution

$$\Delta H^o_{f(\text{propene})} = 20.4 \frac{kJ}{mol} \tag{4.E.1574}$$

$$\Delta H^o_{f(\text{water})} = -241.8 \frac{kJ}{mol} \tag{4.E.1575}$$

$$\Delta H^o_{f(\text{CH}_3(\text{CH}_2)_2\text{OH})} = -104.6 \frac{kJ}{mol} \tag{4.E.1576}$$

$$\Delta H^o = \Delta H^o_{f(\text{CH}_3(\text{CH}_2)_2\text{OH})} - \Delta H^o_{f(\text{propene})} - \Delta H^o_{f(\text{water})} \tag{4.E.1577}$$

$$= -104.6 \frac{kJ}{mol} - (-241.8 \frac{kJ}{mol}) - 20.4 \frac{kJ}{mol} \tag{4.E.1578}$$

$$= 116.8 \frac{kJ}{mol} > 0$$

It is an endothermic reaction. As a result, a higher temperature is required to maximize the yield of product.

Also, according to the ideal gas law, because the moles of gas are proportional to the volume, and the volume is inverse proportional to the pressure; a higher pressure is required to maximize the yield of product.

Q.61

Suppose heptane and octane form an ideal solution. At 20.0°C, pure heptane has a vapor pressure of $\text{P}_1{}^\circ = 0.0562\ \text{atm}$ while pure octane has a vapor pressure of $\text{P}_2{}^\circ = 0.0145\ \text{atm}$. What is the mole fraction of heptane vapor over a solution of heptane and octane

if the solution contained $0.300\ \text{mol}$ heptane and $0.700\ \text{mol}$ octane?

Solution

Since we have been told to assume the solution is ideal, we can use Raoult's law to obtain the partial pressures of heptane and octane, respectively.

$$P_{\text{heptane}} = \left(\frac{0.300\ \text{mol}}{0.300\ \text{mol} + 0.700\ \text{mol}}\right) \times (0.0562\ \text{atm}) = 0.01686\ \text{atm}$$

$$P_{\text{octane}} = \left(\frac{0.700\ \text{mol}}{0.300\ \text{mol} + 0.700\ \text{mol}}\right) \times (0.0145\ \text{atm}) = 0.01015\ \text{atm}$$

Using the relationship between partial pressure and mole fraction, we can obtain the mole fraction of heptane over the solution. Partial pressure and mole fraction can be related through the ideal gas law $P = n\frac{RT}{V}$. Which shows that under constant temperature and pressure, pressure and number of moles are directly related.

$$\chi_{\text{heptane}} = \left(\frac{0.01686\ \text{atm}}{0.01686\ \text{atm} + 0.01015\ \text{atm}}\right) = 0.624$$

Q.63

At 50°C, benzene (C_6H_6) has a vapor pressure of 42.5 kPa and isobutene (C_3H_8) has a vapor pressure of 0.83 torr. When 10.0 g of benzene and 30 g of isobutene are mixed in a solution, they form a nearly ideal solution.

a. Calculate the mole fraction of benzene in the solution.
b. What is the total vapor pressure above the solution in kPa at 50°C ?
c. Calculate the mole fraction of isobutene that exists above the solution in the vapor phase.

Solution

The mole fraction is equal to:

$$\left(\frac{X_A\ mol}{X_A + X_B\ mol}\right)$$

Use dimensional analysis to convert grams to moles:

$$(10.0\ \cancel{g\ C_6H_6})\left(\frac{1\ mol}{78.108\ \cancel{g\ C_6H_6}}\right) = 0.128\ mol$$

$$(30.0\ \cancel{g\ C_3H_8})\left(\frac{1\ mol}{44.094\ \cancel{g\ C_3H_8}}\right) = 0.680\ mol$$

Let:

$X_A =$ the moles of ${}_6CH_6 = 0.128\ \ mol$, $X_B =$ the moles of ${}_3CH_8 = 0.680\ \ mol$,

$$\chi_B = \frac{0.0929\ kPa}{6.81\ kPa} = 0.0136$$

Plug into the equation and solve:

$$\left(\frac{0.128\ mol}{0.128 + 0.680\ mol}\right) = 0.158$$

b) Since the problem states that the result of mixing the two solutions is nearly ideal, we can assume an ideal solution is formed and use Raoult's Law and we can choose to keep pressure in units of kPa OR torr.

It's Raoult's Law:

$P_A = \chi_A \times P_A^o$

Here we have chosen to use units of kPa:

$$P_{C_6H_6} = \chi_{C_6H_6} \times P^o_{C_6H_6}$$

$$P_{C_6H_6} = 0.158 \times 42.5\ kPa = 6.72\ kPa$$

To convert torr to kPa:

$$(0.83\ \cancel{torr}) \left(\frac{0.133\ kPa}{1\ \cancel{torr}} \right) = 0.1104\ kPa$$

$$P_{C_3H_8} = \chi_{C_3H_8} \times P^o_{C_3H_8}$$

$$P_{C_3H_8} = 0.842 \times 0.1104\ kPa = 0.0929\ kPa$$

Then we add these up to find the total pressure:

$$P_{\text{Total}} = \chi_A P_A^o + \chi_B P_B^o$$

$$P_{\text{Total}} = 6.72\ kPa + 0.0929\ kPa\ = 6.81\ kPa$$

c) To find the mole fraction of isobutene **only** in the vapor phase, we can use partial pressure to represent the amount of gas, becase in mixed gas $n \propto p$:

$$\chi_{\text{isobutene}} = \frac{n_{\text{isobutene}}}{n_{\text{tot}}} = \frac{P_{\text{isobutene}}}{P_{\text{tot}}} = \frac{0.83\,\text{torr}}{6.81\,\text{kPa}} = 0.0162$$

Q.65

A solution is prepared by mixing 2g of $\text{CaCl}_2\,(\text{s})$, 2g of $\text{MgCl}_2\,(\text{s})$, and 3g of $\text{MnO}_2\,(\text{s})$ in enough water to make a total volume of 150 mL. Calculate the concentration of chlorine in the solution in grams per liter.

Solution

$m_{\text{Cl}} = 2g\ \text{CaCl}_2(\frac{2(35.5g\ \text{Cl})}{110.98g\ \text{CaCl}_2}) + 2g\ \text{MgCl}_2(\frac{2(35.5g\ \text{Cl})}{95.12g\ \text{MgCl}_2})$

$m_{\text{Cl}} = 2.77g\ \text{Cl}$

mass of chlorine per liter: $\frac{2.77g\ \text{Cl}}{150\times10^{-3}L} = 18.5\frac{g}{L}$

Q.69

Chromium ion, Cr^{2+}, is a good reducing agent, often being itself turned into Cr^{3+}. Suppose that 10 mL of 0.1 M Cr(OH)_2 was needed to reduce completely an 0.05 grams of unknown substance X.

a. If each molecule of X accept just one electron, what is the molecular weight of X?
b. If each molecule of X accept five electrons, what is the molecular weight of X?

Solution

(a) Number of moles of Cr(OH)_2 used = $M \times V$

$= 0.1 \times 10\ \text{mL} = 1\ \text{mmol} = 10^{-3}\ \text{moles}$

Since only one mole of X was used for every mole of Chromium Hydroxide, the number of moles reacted are equal.

$\frac{\text{Mass}}{\text{Molar mass}}$ = number of moles, hence for X,

$\frac{0.05\text{ g}}{(0.01\text{L}\times 0.1\text{M})} = 50\frac{\text{g}}{\text{mol}}$

(b) $\frac{0.05\text{ g}}{(0.01\text{L}\times 0.1\text{M}\times 5)} = 10\frac{\text{g}}{\text{mol}}$

Q.71

A 0.200 g sample of chloride with unknown purity was dissolved in 200 mL of water was then titrated with AgNO_3 solution with a molarity of 0.1 M. After the titration it was determined that 28 mL of AgNO_3 was required to fully titrate the sample of chloride. What's the mass percent of chloride in the original dry sample?

Solution

First write the precipitation reaction:

$$\text{Ag}^+\,(\text{aq}) + \text{Cl}^-\,(\text{aq}) \longrightarrow \text{AgCl}\,(\text{s})$$

Next we need to determine the amount of moles of Ag used during the titration:

$$\text{mol Ag}^+ = 28\,\cancel{mL}\left(\frac{1\,\cancel{L}}{1000\,\cancel{mL}}\right)\left(\frac{0.1\text{ mol}}{1\,\cancel{L}}\right) = 2.80\times 10^{-3}\text{ mol Ag}^+$$

Now that we know the amount of moles of Ag reacted because Ag and Cl combine at a one to one ration we can find the mass of Cl used:

$$\text{mass Cl}^- = 2.80\times 10^{-3}\,\cancel{mol}\left(\frac{35.45\text{ g}}{1\,\cancel{mol}}\right) = 9.92\times 10^{-2}\text{ g Cl}^-$$

Now that we know the mass of Cl in the unknown we can calculate the mass percent:

$$100\left(\frac{0.0992\text{ g}}{0.2\text{g}}\right) = 49.63$$

Q.73

At 20°C, the vapor pressure of pure water is 17.5 mmHg. When 110 g of a substance X_y is dissolved in 500 g of water, the vapor pressure of the solution is 15.0 mmHg. Given that this substance has a molecular mass of 12.011 g/mol, what is the molecular formula of this substance X_y. (i.e. what is the number value of subscript y).

Solution

For this question, we can use Raoult's Law

$$P_{\text{solution}} = \chi_{\text{solvent}} \times P°_{\text{solvent}}$$

First, we plug in the known values of the pressure of the solution and the pressure of the pure solvent, water, to find the mole fraction.

$$15.0\ \text{ mmHg} = \chi_{\text{solvent}} \times 17.5\ \text{ mmHg}$$

$$\chi_{\text{solvent}} = 0.8571$$

Next, we can calculate the the number of moles of the solvent from its mass and molecular weight.

$$\text{Moles of solvent} = 500\ \text{ g} \times \frac{1}{18.015\text{ g/mol}} = 27.75\ \text{ moles}$$

Next, we can calculate the moles of the solute from the mole fraction of the solvent

$$0.8571 = \frac{27.75 \text{ moles}}{27.75 \text{ moles } + \text{ moles of } X_y}$$

$$\text{moles of } X_y = 4.63 \text{ moles}$$

From here, we can calculate the molecular formula of the substance by dividing the amount of grams per mole used in the solution by the molecular mass of the substance.

$$\frac{110 \text{ g}}{4.63 \text{ moles}} = 23.76 \text{ g/mol}$$

$$(23.76 \text{ g/mol}) \times (\frac{1}{12.011 \text{ g/mol}}) = 1.98$$

$$1.98 \approx 2$$

Thus, the molecular formula of our substance is $\mathrm{X_2}$.

Q.81

The cell membrane of a plant cell is permeable to water. In a salt solution, the plant cells shrivel (lose water) when the concentration is high, and swell (take up water) when the concentration is low. Scientists perform an experiment at 30°C, where an aqueous solution of NaCl with a freezing point of -0.028°C is used to water the plant cells. This causes the plant cells to neither swell nor shrink indicating that the osmotic pressure of the plant cell contents is equal to that of the NaCl solution. Assuming the molarity and molality of the plant cell contents are equal, calculate the osmotic pressure of the solution inside the plant cells. The K_f for the solution is $1.86 \frac{\text{K kg}}{\text{mol}}$.

Solution

Plug in the given values into the equation for freezing point depression to solve for the molality of the solution

$$\Delta T_f = -K_f m$$

$$-0.0218 = -1.86 K \cdot kg \cdot mol^{-1} m$$

$$m = 0.015 \frac{kg}{mol}$$

Because the plant cell neither swells nor shrinks, the molality of the solution is equivalent to the molality of the plant cell contents. According to the question, assume the molarity and molality are equal so concentration

$$c = 0.15 M$$

Use the following equation to calculate for the osmotic pressure, π.

$$\begin{aligned} \pi &= cRT \\ &= (0.15M)(0.08206 \frac{L \ atm}{mol \ K})(303.15K) \\ &= 0.374 atm \end{aligned}$$

Q.83

Jim loves the smell of grass. He loves it so much that he frequently sniffs the fumes from 1-Hexanol, which is a chemical compound that is known to smell like grass trimmings. Because of his love, he decides to make his garage into a “gas den”, and aimed to have 60% of the air in it as 1-Hexanol gas. He achieves this by filling a pool with a mixture of 1-Hexanol and Water. Assume that the air in the “gas den” consists of only the fumes from this mixture. If the pool has 10000L of water in it, how many litres of 1-Hexanol does he need? Use Henry’s Law to determine this amount.

Relevant Information:

1-Hexanol:

- Density: $814\frac{kg}{m^3}$
- Molar mass: $107.1748\frac{g}{mol}$
- Henry's Law Constant: $64\frac{molal}{bar}$

Water:

- Density: $1000\frac{kg}{m^3}$

Solution

This problem asks for the amount, in litres, of 1-Hexanol that is required to make Jim's dreams come true. The information given is the density of 1-Hexanol and its molar mass, but since they don't have very much to do with pressure, they can be set aside for now. The question explicitly mentions that Henry's Law should be used, so start be identifying what Henry's Law actually does:

$$C = kP$$

Where C is concentration, k is Henry's Law constant, and P is partial pressure. The question gives out the fact that Jim wants the air in his garage to be 60% 1-Hexanol vapor. Remember the total pressure of air is 1 atm ≈ 1 bar (ignore the error here). Therefore, the partial pressure of 1-hexanol is $1\ \text{bar} \times 60\% = 0.6\ \text{bar}$. The Henry's Law constant is also provided, and by plugging those two in, the concentration of 1-Hexanol in the desired "solution" (more accurately, giant pool of chemicals) is found. This process is shown below:

$$C = kP = (64\frac{molal}{bar}) \times 0.6\,\text{bar} = 38.4$$

This concentration, from the units of k, is in mo*lality,* which is $\frac{mol_{\text{solute}}}{kg_{\text{solvent}}}$. Now all that is left is to convert molality to litres. By utilizing the molar mass of 1-Hexanol:

$$38.4\frac{mol_{\text{solute}}}{kg_{\text{solvent}}} \times 107.1748\frac{g}{mol} \approx 4115.51\frac{g_{\text{solute}}}{kg_{\text{solvent}}}$$

We know that the solvent is water, and that water has a density of $1000\frac{kg}{m^3}$. Also, the conversion rate of m^3 to L is 1:1000. Therefore, the equation can be solved as follows.

$$4115.51\frac{g_{\text{solute}}}{kg_{\text{solvent}}} \times 1000\frac{kg_{\text{H}_2\text{O}}}{m^3} \times \frac{m^3}{1000\,L_{\text{H}_2\text{O}}} \approx 4115.51\frac{g_{\text{solute}}}{L_{\text{solvent}}}$$

We now have the value for how many grams of solute (1-Hexanol) there should be per litre of solvent. simply divide this value by the density to obtain litres of 1-Hexanol per litre of water. Multiply this number by the amount of water in the pool to get the desired amount of solute that is needed for the solution! (note that the density was converted to $\frac{g}{L}$,

$$4115.51\frac{g_{\text{solute}}}{L_{\text{solvent}}} \div \left(814000\frac{g_{\text{1-hexanol}}}{L}\right) \times 10000 L_{\text{H}_2\text{O}} = 50.56\,\text{L}$$

~~Therefore, Jim needs 50,560L of 1-Hexanol to put in his pool. That's going to take a big pool!~~

Therefore, Jim needs 50.56L of 1-Hexanol to put in his pool.

Please note that, while various units do appear in the conversions, H_2O can be considered as solute and 1-Hexanol as the solvent, so the units can cancel.

Abstract: Utilize henry's law to find concentration (molality). From that, convert molality to g_{solute} to L_{solute}.

Q.87

A 3.5 gram sample is decomposed into a compound containing nitrogen, hydrogen, and oxygen, together creating 4.00 g of NO_2 and 7.00 g of H_2O. The molar mass of the sample is $78.5 \frac{g}{mol}$. Find the molecular formula of this sample.

Solution

First, the moles of each Nitrogen, Hydrogen, and Oxygen in solution are calculated:

$mol_N = 4g\ NO_2 \times (\frac{1\ mol\ NO_2}{46.005 \frac{g}{mol}}) \times (\frac{1\ mol\ N}{1\ mol\ NO_2}) = 0.0869\ mol$

$mass_N = (14.00 \frac{g}{mol})(0.0869 mol) = 1.2172g\ N$

$mol_H = 7g\ H_2O \times (\frac{1\ mol\ H_2O}{18.02 \frac{g}{mol}}) \times (\frac{2\ mol\ H}{1\ mol\ H_2O}) = 0.7769\ mol$

$mass_H = (1.01 \frac{g}{mol})(0.7769 mol) = 0.7847g\ H$

From these values, moles of O can be calculated to be:

$3.5\ gram\ sample = grams_N + grams_H + grams_O$

$3.5 = 1.2172g + 0.7847g + grams_O$

$grams_O = 1.4981g$

$mol_O = \frac{1.4981g}{15.9994 \frac{g}{mol}} = 0.0936\ mol$

The mole values for each element create a ratio of $H_{0.7769}\ N_{0.0869}\ O_{0.0936}$, creating an empirical formula H_9NO

From here, the molecular formula can be established using the molar mass:

$\text{Empirical formula mass} = 9(1.01 \frac{g}{mol\ H}) + (14.00 \frac{g}{mol\ N}) + (15.9994 \frac{g}{mol\ O})$

$\text{Empirical formula mass} = 39.0894 \frac{g}{mol}$

$\text{Sample Mass} = 78.5 \frac{g}{mol}$

$\frac{78.5 \frac{g}{mol}}{39.084 \frac{g}{mol}} = 2.00$

$2(H_9NO) = H_{18}N_2O_2 = \text{Molecular Formula}$

Q.87

5 grams of a substance containing hydrogen, carbon and oxygen were fully combusted and produced 3.00 grams of H_2O and 7.33 grams of CO_2. When 10.64 grams of the substance was mixed with 0.5 kg of water, the freezing point was found to decrease by 0.0605°C. What is the substance?

Solution

The generic equation for this reaction is

$$C_x\ H_y\ O_z + O_2 \longrightarrow H_2O + CO_2$$

The molar masses of carbon, hydrogen, and oxygen are 12.01 g/mol, 1.008 g/mol, and 16.00 g/mol respectively. Therefore the molar masses of water and carbon dioxide are $18.016 \frac{g}{mol}$ and $44.01 \frac{g}{mol}$. These values can be used to determine the mass percent of hydrogen in water

$$\frac{2(1.008)\ \frac{g}{mol}}{18.016\ \frac{g}{mol}} \times 100 = 11.2\%$$

And the mass percent of carbon in carbon dioxide

$$\frac{12.01\ \frac{g}{mol}}{44.01\ \frac{g}{mol}} \times 100 = 27.3\%$$

The mass percents can be used to determine the amount of hydrogen and carbon are present.

$$3.00\ g \times 0.112 = 0.336\ g \text{ of Hydrogen}$$

$$7.33\ g \times 0.273 = 2.001\ g \text{ of Carbon}$$

By subtracting the masses of Carbon and Hydrogen from the original mass of the substance, the mass of oxygen present in the substance can be found

$$5\ g - (0.336\ g + 2.001\ g) = 2.663\ g \text{ of Oxygen}$$

By dividing the masses present by the molar mass, the amount of moles of each element can be determined

$$\frac{0.112\ g}{1.008\ \frac{g}{mol}} = 0.333\ mol \text{ of Hydrogen}$$

$$\frac{2.001\ g}{12.01\ \frac{g}{mol}} = 0.167\ mol \text{ of Carbon}$$

$$\frac{2.663\ g}{16.00\ \frac{g}{mol}} = 0.166\ mol \text{ of Oxygen}$$

By looking at the amount of moles of each element, it can be noticed that there are equal amounts of carbon and oxygen and twice as much hydrogen as carbon or oxygen. Therefore the ratio of $\mathrm{C:H:O}$ in the substance is $1:2:1$. However, the molar mass of the substance remains unknown, but it can be found using the information about the freezing point depression.

From the formula for freezing point depression

$$\Delta T = -i \times k_f \times m$$

$$-0.0605°C = -1 \times 0.512°C\ m^{-1} \times m$$

$$m = \frac{0.0605°C}{0.512\frac{°C}{m}} = 0.118\ \frac{mol}{kg}$$

By multiply by the mass of solvent (water), we can determine the amount of moles that was dissolved in the water

$$0.118\ \frac{mol}{kg} \times 0.5\ kg = 0.059\ mol$$

The last step in finding the molar mass of the substance is to divide the mass dissolved by the moles dissolved

$$\frac{10.64\ g}{0.059\ mol} = 180.3\ \frac{g}{mol}$$

Now we can find the formula of the substance. The first step is to find the number of moles of the substance combusted

$$\frac{5\ g}{180.3\ \frac{g}{mol}} = 0.0277\ mol$$

We can compare this to the number of carbon moles combusted to determine the number of carbon atoms per molecule of the substance

$$\frac{0.167\ g\ \text{of Carbon}}{0.0277\ mol} = 6\ \text{Carbon atoms}$$

When we apply the number of carbon atoms to the ratio of elements found earlier, the chemical formula comes to be $C_6H_{12}O_6$ which is glucose.

Answer: Glucose

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UNIT III: CHEMICAL EQUILIBRIA

Chemical equilibrium is a state in which the rate of the forward reaction equals the rate of the backward reaction. In other words, there is no net change in concentrations of reactants and products. This kind of equilibrium is also called dynamic equilibrium and can be used in a wide range of processes including both chemical and physical changes. An equilibrium is a situation whereby the quantity or quality of the sample does not change in time. Such a situation is intimately connected to "thermodynamics" as discussed in previously. As you will learn in Chem 2CH, electrochemistry is the third member of this troika.

V: Chemical Equilibrium

5.1: The Nature of Chemical Equilibrium
5.2: The Empirical Law of Mass Action
5.3: Thermodynamic Description of the Equilibrium State
5.4: The Law of Mass Action for Related and Simultaneous Equilibria
5.5: Gas-Phase and Heterogeneous Reaction Equilibria
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V: CHEMICAL EQUILIBRIUM

Chemical equilibrium is the state in which both reactants and products are present in concentrations which have no further tendency to change with time. This results when the forward reaction proceeds at the same rate as the reverse reaction. Thus, no net changes in the concentrations of the reactant(s) and product(s) are observed. This is known as dynamic equilibrium

5.1: The Nature of Chemical Equilibrium

5.2: The Empirical Law of Mass Action

5.3: Thermodynamic Description of the Equilibrium State

5.4: The Law of Mass Action for Related and Simultaneous Equilibria

5.5: Gas-Phase and Heterogeneous Reaction Equilibria

5.6: The Direction of Change in Chemical Reactions: Empirical Description

5.7: The Direction of Change in Chemical Reactions - Thermodynamic Explanation

5.8: Distribution between Immiscible Phases - Extraction and Separation Processes

5.E: Chemical Equilibrium (Exercises)

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5.1: The Nature of Chemical Equilibrium

Learning Objectives

- To understand what is meant by chemical equilibrium.

In the last chapter, we discussed the principles of chemical kinetics, which deal with the *rate of change*, or how quickly a given chemical reaction occurs. We now turn our attention to the *extent* to which a reaction occurs and how reaction conditions affect the final concentrations of reactants and products. For most of the reactions that we have discussed so far, you may have assumed that once reactants are converted to products, they are likely to remain that way. In fact, however, virtually all chemical reactions are *reversible* to some extent. That is, an opposing reaction occurs in which the products react, to a greater or lesser degree, to re-form the reactants. Eventually, the forward and reverse reaction rates become the same, and the system reaches **chemical equilibrium,** the point at which the composition of the system no longer changes with time.



Figure 5.1.1: Dinitrogen tetroxide is a powerful oxidizer that reacts spontaneously upon contact with various forms of hydrazine, which makes the pair a popular propellant combination for rockets. Nitrogen dioxide at –196 °C, 0 °C, 23 °C, 35 °C, and 50 °C. (NO_2) converts to the colorless dinitrogen tetroxide (N_2O_4) at low temperatures, and reverts to NO_2 at higher temperatures. (CC BY-SA 3.0; Eframgoldberg).

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide (N_2O_4) to nitrogen dioxide (NO_2). You may recall that NO_2 is responsible for the brown color we associate with smog. When a sealed tube containing solid N_2O_4 (mp = –9.3°C; bp = 21.2°C) is heated from –78.4°C to 25°C, the red-brown color of NO_2 appears (Figure 5.1.1). The reaction can be followed visually because the product (NO_2) is colored, whereas the reactant (N_2O_4) is colorless:



The double arrow indicates that both the forward reaction



and reverse reaction



occurring simultaneously (i.e, the reaction is reversible). However, this does not necessarily mean the system is equilibrium as the following chapter demonstrates.

Figure 5.1.2 shows how the composition of this system would vary as a function of time at a constant temperature. If the initial concentration of NO_2 were zero, then it increases as the concentration of N_2O_4 decreases. Eventually the composition of the system stops changing with time, and chemical equilibrium is achieved. Conversely, if we start with a sample that contains no N_2O_4 but an initial NO_2 concentration twice the initial concentration of N_2O_4 (Figure 5.1.2a), in accordance with the stoichiometry of the reaction, we reach exactly the same equilibrium composition (Figure 5.1.2b). Thus equilibrium can be approached from either direction in a chemical reaction.

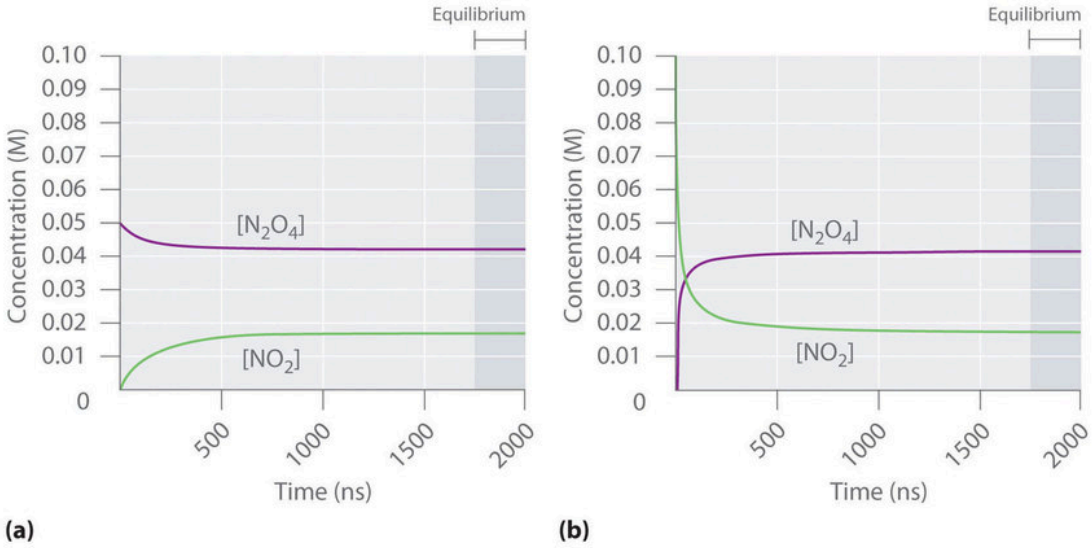


Figure 5.1.2: The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system contains 0.1000 M NO_2 and no N_2O_4. The concentration of NO_2 decreases with time as the concentration of N_2O_4 increases. In both cases, the final concentrations of the substances are the same: $[N_2O_4]$ = 0.0422 M and $[NO_2]$ = 0.0156 M at equilibrium. (CC BY-SA-NC; Anonymous by request)

Figure 5.1.3 shows the forward and reverse reaction rates for a sample that initially contains pure NO_2. Because the initial concentration of N_2O_4 is zero, the forward reaction rate (dissociation of N_2O_4) is initially zero as well. In contrast, the reverse reaction rate (dimerization of NO_2) is initially very high ($2.0 \times 10^6\ M/s$), but it decreases rapidly as the concentration of NO_2 decreases. As the concentration of N_2O_4 increases, the rate of dissociation of N_2O_4 increases—but more slowly than the dimerization of NO_2—because the reaction is only first order in N_2O_4 (rate = $k_f[N_2O_4]$, where k_f is the rate constant for the forward reaction in Equations 1.1.1 and 5.1.1128). Eventually, the forward and reverse reaction rates become identical, $k_f = k_r$, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at different rates, then the system is not at equilibrium.

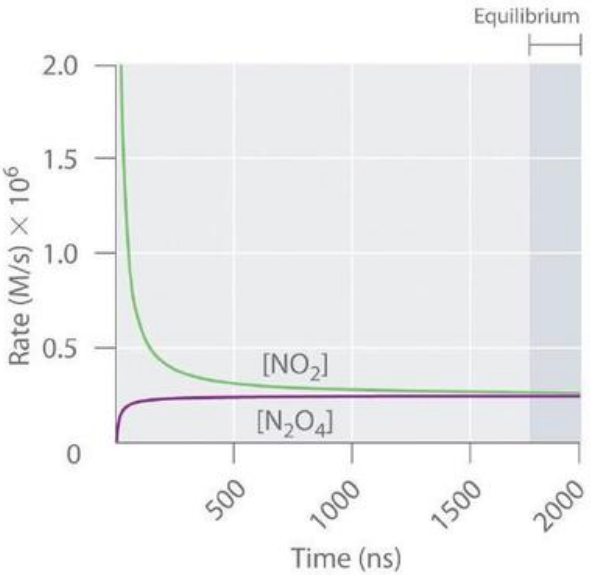


Figure 5.1.3: The Forward and Reverse Reaction Rates as a Function of Time for the $N_2O_{4(g)} \diamondsuit 2NO_{2(g)}$ System Shown in Part (b) in Figure 5.1.2. (CC BY-SA-NC; Anonymous by request)

The rate of dimerization of $\mathrm{NO_2}$ (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of $\mathrm{N_2O_4}$ is zero, the rate of the dissociation reaction (forward reaction) at $t = 0$ is also zero. As the dimerization reaction proceeds, the $\mathrm{N_2O_4}$ concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of $\mathrm{N_2O_4}$ and $\mathrm{NO_2}$ no longer change.

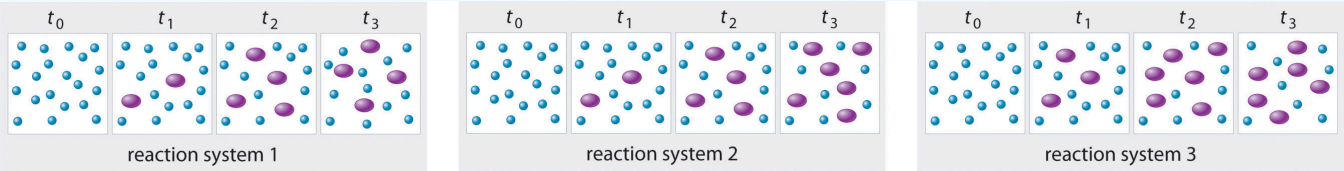
At equilibrium, the forward reaction rate is equal to the reverse reaction rate.

Example 5.1.1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation:

$$2A \rightleftharpoons B$$

where the blue circles are A and the purple ovals are B. Each set of panels shows the changing composition of one of the three reaction mixtures as a function of time. Which system took the longest to reach chemical equilibrium?



In reaction system 1 theree are four purple ovals at t3. In reaction system 2 there are size purple ovals at t3. In reaction system systems there are six ovals at t2 and t3.

Given: three reaction systems

Asked for: relative time to reach chemical equilibrium

Strategy:

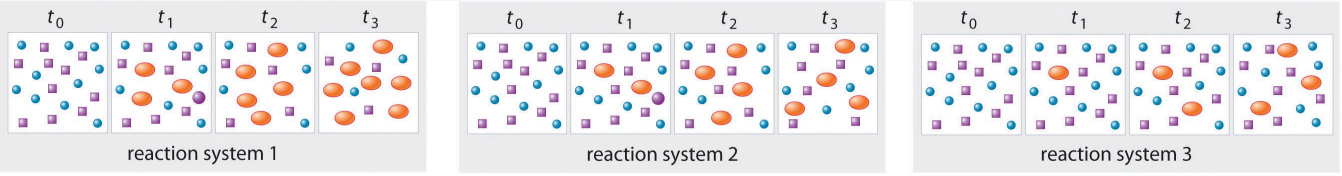
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

Solution:

In systems 1 and 3, the concentration of A decreases from t_0 through t_2 but is the same at both t_2 and t_3. Thus systems 1 and 3 are at equilibrium by t_3. In system 2, the concentrations of A and B are still changing between t_2 and t_3, so system 2 may not yet have reached equilibrium by t_3. Thus system 2 took the longest to reach chemical equilibrium.

Exercise 5.1.1

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B ⇌ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?



In reaction system 1 there are seven orange ovals at t3. In reaction system two there are four orange ovals at t3. In reaction system three there are three orange ovals at t3.

Answer

system 2

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online
https://www.youtube.com/embed/4AJbFuzW2cs?vq=hd1080

A Video Introduction to Dynamic Equilibrium: Introduction to Dynamic Equilibrium(opens in new window) [youtu.be]

Summary

At equilibrium, the forward and reverse reactions of a system proceed at equal rates. Chemical equilibrium is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

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5.2: The Empirical Law of Mass Action

Learning Objectives

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.
- To understand how different phases affect equilibria.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the decomposition reaction of $\mathrm{N_2O_4}$ to $\mathrm{NO_2}$. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

[redacted]

and

[redacted]

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

[redacted]

so

[redacted]

The ratio of the rate constants gives us a new constant, the **equilibrium constant** (K), which is defined as follows:

[redacted]

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.

> The equilibrium constant is equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction.

Table 5.2.1 lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 1.1.1. At equilibrium the magnitude of the quantity $[\mathrm{NO_2}]^2/[\mathrm{N_2O_4}]$ is essentially the same for all five experiments. In fact, no matter what the initial concentrations of $\mathrm{NO_2}$ and $\mathrm{N_2O_4}$ are, at equilibrium the quantity $[\mathrm{NO_2}]^2/[\mathrm{N_2O_4}]$ will always be $6.53 \pm 0.03 \times 10^{-3}$ at 25°C, which corresponds to the ratio of the rate constants for the forward and reverse reactions (Equation 2.5.998). That is, at a given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of the reactants and products vary depending on their initial concentrations.

Table 5.2.1: Initial and Equilibrium Concentrations for $NO_2 : N_2O_4$ Mixtures at 25°C

	Initial Concentrations		Concentrations at Equilibrium		
Experiment	**[N_2O_4] (M)**	**[NO_2] (M)**	**[N_2O_4] (M)**	**[NO_2] (M)**	$K = [NO_2]^2/[N_2O_4]$
1	0.0500	0.0000	0.0417	0.0165	6.54×10^{-3}
2	0.0000	0.1000	0.0417	0.0165	6.54×10^{-3}

Experiment	Initial Concentrations		Concentrations at Equilibrium		
	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
3	0.0750	0.0000	0.0647	0.0206	6.56×10^{-3}
4	0.0000	0.0750	0.0304	0.0141	6.54×10^{-3}
5	0.0250	0.0750	0.0532	0.0186	6.50×10^{-3}

Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction of the general form

[redacted]

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action and can be stated as follows:

[redacted]

where K is the equilibrium constant for the reaction. Equation 2.5.1009 is called the equilibrium equation, and the right side of Equation 5.2.1130 is called the equilibrium constant expression. The relationship shown in Equation 5.2.1130 is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of K shown in Table 5.2.2, for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reductant and Cl_2 is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of K less than 10^{-3} indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

*Table [redacted]: Equilibrium Constants for Selected Reactions**

Reaction	Temperature (K)	Equilibrium Constant (K)
$S(s) + O_2(g) \rightleftharpoons SO_2(g)$	300	4.4×10^{53}
$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g)$	500	2.4×10^{47}
$H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g)$	300	1.6×10^{33}
$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$	300	4.1×10^{18}
$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$	300	4.2×10^{13}
$3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$	300	2.7×10^{8}
$H_2(g) + D_2(g) \rightleftharpoons 2\,HD(g)$	100	1.92
$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$	300	2.9×10^{-1}
$I_2(g) \rightleftharpoons 2\,I(g)$	800	4.6×10^{-7}
$Br_2(g) \rightleftharpoons 2\,Br(g)$	1000	4.0×10^{-7}
$Cl_2(g) \rightleftharpoons 2\,Cl(g)$	1000	1.8×10^{-9}

***Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.**

Reaction	Temperature (K)	Equilibrium Constant (K)
$F_2(g) \rightleftharpoons 2F(g)$	500	7.4×10^{-13}
***Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.**		

You will also notice in Table 5.2.2 that equilibrium constants have no units, even though Equation 5.2.1130 suggests that the units of concentration might not always cancel because the exponents may vary. **In fact, equilibrium constants are calculated using "effective concentrations," or activities, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M.** As shown in Equation 5.2.1131, the units of concentration cancel, which makes K unitless as well:

[redacted]

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

[redacted]

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]} \tag{5.2.1579}$$

with K varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of H_2, D_2, and HD contains significant concentrations of both product and reactants.

Figure 5.2.1 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants \rightleftharpoons products. Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equations 5.2.1131 and 5.2.1130), when $k_f \gg k_r$, K is a **large** number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f \ll k_r$, K is a very **small** number, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium.

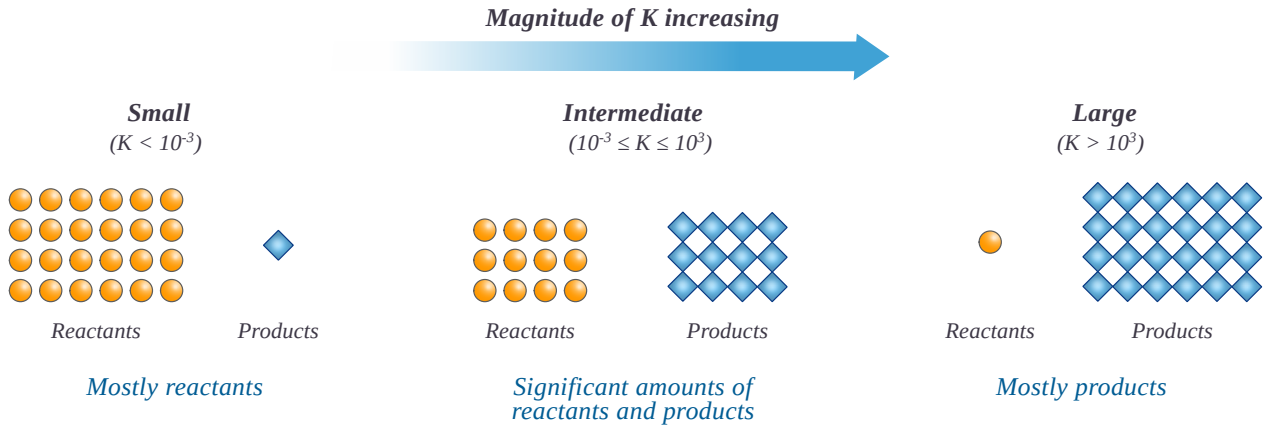


Figure 5.2.1: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium. (CC BY-NC; Ümit Kaya)

A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.

Example 5.2.1

Write the equilibrium constant expression for each reaction.

- $\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$
- $\mathrm{CO\,(g) + \frac{1}{2}\,O_2\,(g) \rightleftharpoons CO_2\,(g)}$
- $\mathrm{2\,CO_2\,(g) \rightleftharpoons 2\,CO(g)^{+}O_2\,(g)}$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 5.2.1130. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

The only product is ammonia, which has a coefficient of 2. For the reactants, N_2 has a coefficient of 1 and $\mathrm{H_2}$ has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[NH_3]^2}{[N_2][H_2]^3}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and $\mathrm{O_2}$, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[CO_2]}{[CO][O_2]^{1/2}}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for $\mathrm{O_2}$. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2:

$$\frac{[CO]^2[O_2]}{[CO_2]^2}$$

Exercise 5.2.1

Write the equilibrium constant expression for each reaction.

a. $\mathrm{N_2O\,(g) \rightleftharpoons N_2\,(g) + \frac{1}{2}\,O_2\,(g)}$
b. $\mathrm{2\,C_8H_{18}\,(g) + 25\,O_2\,(g) \rightleftharpoons 16\,CO_2\,(g) + 18\,H_2O\,(g)}$
c. $\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)}$

Answer a

$$K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$$

Answer b

$$K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$$

Answer c

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

Example 5.2.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Given: systems and values of K

Asked for: composition of systems at equilibrium

Strategy:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

a. Only system 4 has $K >> 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K << 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise 5.2.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

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

Values of the equilibrium constant at various temperatures were reported as

- $K_{25°C} = 3.3 \times 10^8$,
- $K_{177°C} = 2.6 \times 10^3$, and
- $K_{327°C} = 4.1$.

a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
b. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer a

327°C, where K is smallest

Answer b

25°C

Variations in the Form of the Equilibrium Constant Expression

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 2.5.1009 in reverse, we obtain the following:



The corresponding equilibrium constant K' is as follows:



This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is as follows:



but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K′ is given by the inverse expression:



Consider another example, the formation of water: $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$. Because H_2 is a good reductant and O_2 is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form O_2 and H_2, is very small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into H_2 and O_2.

> The equilibrium constant for a reaction written in reverse is the *inverse* of the equilibrium constant for the reaction as written originally.

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, we could write the equation for the reaction

$$2NO_2 \rightleftharpoons N_2O_4 \tag{5.2.1580}$$

as

$$NO_2 \rightleftharpoons \frac{1}{2}N_2O_4 \tag{5.2.1581}$$

with the equilibrium constant K″ is as follows:



The values for K′ (Equation 5.2.1137) and K″ are related as follows:

[redacted]

In general, if all the coefficients in a balanced chemical equation were subsequently multiplied by n, then the new equilibrium constant is the original equilibrium constant raised to the nth power.

Example 5.2.3: The Haber Process

At 745 K, K is 0.118 for the following reaction:

$$\mathrm{N_2\,(g) + 3\,H_2\,(g)} \rightleftharpoons \mathrm{2\,NH_3\,(g)}$$

What is the equilibrium constant for each related reaction at 745 K?

a. $\mathrm{2\,NH_3\,(g)} \rightleftharpoons \mathrm{N_2\,(g) + 3\,H_2\,(g)}$
b. $\mathrm{\frac{1}{2}\,N_2\,(g) + \frac{3}{2}\,H_2\,(g)} \rightleftharpoons \mathrm{NH_3\,(g)}$

Given: balanced equilibrium equation, K at a given temperature, and equations of related reactions

Asked for: values of K for related reactions

Strategy:

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate K for each reaction.

Solution:

The equilibrium constant expression for the given reaction of $\mathrm{N_2\,(g)}$ with $\mathrm{H_2\,(g)}$ to produce $\mathrm{NH_3\,(g)}$ at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118$$

This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47$$

In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344$$

Exercise

At 527°C, the equilibrium constant for the reaction

$$\mathrm{2\,SO_2\,(g) + O_2\,(g)} \rightleftharpoons \mathrm{2\,SO_3\,(g)}$$

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$\mathrm{SO_3\,(g)} \rightleftharpoons \mathrm{SO_2\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)}$$

Answer

3.6×10^{-3}

Law of Mass Action for Gas-Phase Reactions

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol K_p is used to denote equilibrium constants calculated from partial pressures. For the general reaction

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons c\,\mathrm{C} + d\,\mathrm{D}$$

in which all the components are gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

[redacted]

Thus K_p for the decomposition of N_2O_4 (Equation 1.1.1) is as follows:

[redacted]

Like K, K_p is a unitless quantity because the quantity that is actually used to calculate it is an "effective pressure," the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity. The "effective pressure" is called the **fugacity**, just as activity is the effective concentration.

Because partial pressures are usually expressed in atmospheres or mmHg, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, the numerical values of K and K_p are usually different. They are, however, related by the ideal gas constant (R) and the absolute temperature (T):

[redacted]

where K is the equilibrium constant expressed in units of concentration and Δn is the difference between the numbers of moles of gaseous products and gaseous reactants ($n_p - n_r$). The temperature is expressed as the absolute temperature in Kelvin. According to Equation 5.2.1144, $K_p = K$ only if the moles of gaseous products and gaseous reactants are the same (i.e., $\Delta n = 0$). For the decomposition of N_2O_4, there are 2 mol of gaseous product and 1 mol of gaseous reactant, so $\Delta n = 1$. Thus, for this reaction,

$$K_p = K(RT)^1 = KRT \tag{5.2.1582}$$

Example 5.2.4: The Haber Process (again)

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:

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

What is K_p for this reaction at the same temperature?

Given: equilibrium equation, equilibrium constant, and temperature

Asked for: K_p

Strategy:

Use the coefficients in the balanced chemical equation to calculate Δn. Then use Equation 5.2.1144 to calculate K from K_p.

Solution:

This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2 - 4) = -2$. We know K, and $T = 745\ \ K$. Thus, from Equation 5.2.1141, we have the following:

$$K_p = K(RT)^{-2} = \frac{K}{(RT)^2} = \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2} = 3.16 \times 10^{-5}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

Exercise 5.2.4:

Calculate K_p for the reaction

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

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer

$$K_p = 1.2 \times 10^3$$

Law of Mass Action for Reactions Involving Pure Substances and Multiple Phases

When the products and reactants of a reaction at equilibrium in a single phase (e.g., liquid, gas or solids of different lattices), the system is a **homogeneous equilibrium**. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system where the reactants and products are in two or more phase is called a **heterogeneous equilibrium** (e.g, the reaction of a gas with a solid or liquid or two different solid lattices in co-existing).

Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, their concentrations are treated as constants, which allows us to simplify equilibrium constant expressions that involve pure solids or liquids.The reference states for pure solids and liquids are those forms stable at 1 bar (approximately 1 atm), which are assigned an activity of 1. (Recall that the density of water, and thus its volume, changes by only a few percentage points between 0 °C and 100 °C.)

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:



The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:



Because graphite is a solid, however, its molar concentration, determined from its density and molar mass, is essentially constant and has the following value:



We can rearrange Equation 5.2.1148 so that the constant terms are on one side:



Incorporating the constant value of $[C]$ into the equilibrium equation for the reaction in Equation 5.2.1149,

[redacted]

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

[redacted]

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the concentrations of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and CO_2, the system described in Equation 5.2.1146 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 5.2.2, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

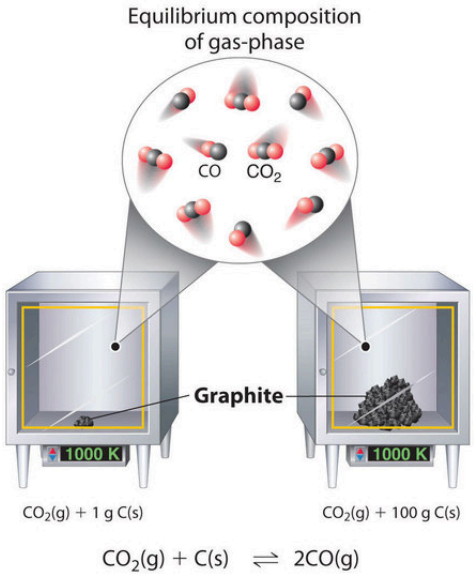


Figure 5.2.2: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

Example 5.2.1

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

a. $PCl_{3(l)} + Cl_{2(g)} \rightleftharpoons PCl_{5(s)}$
b. $Fe_3O_{4(s)} + 4H_{2(g)} \rightleftharpoons 3Fe_{(s)} + 4H_2O_{(g)}$

Given: balanced equilibrium equations

Asked for: expressions for K and K_p

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution

This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their concentrations do not appear in the equilibrium constant expression because they do not change significantly. So

$$K = \frac{1}{[Cl_2]}$$

and

$$K_p = \frac{1}{P_{Cl_2}}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which do not appear in the equilibrium constant expressions. The two gases do, however, appear in the expressions:

$$K = \frac{[H_2O]^4}{[H_2]^4}$$

and

$$K_p = \frac{(P_{H_2O})^4}{(P_{H_2})^4}$$

Exercise 5.2.1

Write the expressions for K and K_p for the following reactions.

a. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
b. $\underset{glucose}{C_6H_{12}O_{6(s)}} + 6O_{2(g)} \rightleftharpoons 6CO_{2(g)} + 6H_2O_{(g)}$

Answer a

$K = [CO_2]$ and $K_p = P_{CO_2}$

Answer b

$$K = \frac{[CO_2]^6[H_2O]^6}{[O_2]^6} \text{ and } K_p = \frac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$$

For reactions carried out in solution, the concentration of the solvent is omitted from the equilibrium constant expression even when the solvent appears in the balanced chemical equation for the reaction. The concentration of the solvent is also typically much greater than the concentration of the reactants or products (recall that pure water is about 55.5 M, and pure ethanol is about 17 M). Consequently, the solvent concentration is essentially constant during chemical reactions, and the solvent is therefore treated as a pure liquid. The equilibrium constant expression for a reaction contains only those species whose concentrations could change significantly during the reaction.

The concentrations of pure solids, pure liquids, and solvents are omitted from equilibrium constant expressions because they do not change significantly during reactions when enough is present to reach equilibrium.

Summary

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.
- Definition of equilibrium constant in terms of forward and reverse rate constants:

$$K = \frac{k_f}{k_r}$$

- Equilibrium constant expression (law of mass action):

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Equilibrium constant expression for reactions involving gases using partial pressures:

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

- Relationship between K_p and K:

$$K_p = K(RT)^{\Delta n}$$

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the equilibrium constant (K), a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same K. For a system at equilibrium, the law of mass action relates K to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the equilibrium equation. The ratio is called the equilibrium constant expression. When a reaction is written in the reverse direction, K and the equilibrium constant expression are inverted. For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures (K_p) is related to K by the ideal gas constant (R), the temperature (T), and the change in the number of moles of gas during the reaction. An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

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5.3: Thermodynamic Description of the Equilibrium State

Learning Objectives

- Gibbs Energy is a state function defined as $G = H–TS$.
- The practical utility of the Gibbs function is that ΔG for any process is negative if it leads to an increase in the entropy of the world. Thus spontaneous change at a given temperature and pressure can only occur when it would lead to a decrease in G.
- The sign of the standard free energy change ΔG^o of a chemical reaction determines whether the reaction will tend to proceed in the forward or reverse direction.
- Similarly, the relative signs of ΔH^o and ΔH^o determine whether the spontaneity of a chemical reaction will be affected by the temperature, and if so, in what way.
- The existence of sharp melting and boiling points reflects the differing temperature dependancies of the free energies of the solid, liquid, and vapor phases of a pure substance, which are in turn reflect their differing entropies.

Previously, we saw that it is the **sum** of the entropy changes of the system and surroundings that determines whether a process will occur spontaneously. In chemical thermodynamics we prefer to focus our attention on the system rather than the surroundings, and would like to avoid having to calculate the entropy change of the surroundings explicitly.

In this unit we introduce a new thermodynamic function, the *free energy*, which turns out to be the single most useful criterion for predicting the direction of a chemical reaction and the composition of the system at equilibrium. However, the term "free energy", although still widely used, is rather misleading, so we will often refer to it as "Gibbs energy." The free energy enables us to do this for changes that occur at a constant temperature and pressure (the *Gibbs energy*) or constant temperature and volume (the *Helmholtz energy*.)

Free energy: the Gibbs function

The Gibbs energy (also known as the *Gibbs function* or *Gibbs Potential*) is defined as

[redacted]

in which S refers to the entropy of the *system*. Since H, T and S are all state functions, so is G. Thus for any change in state (under constant temperature), we can write the extremely important relation

[redacted]

How does this simple equation encompass the entropy change of the world ΔS_{total}, which we already know is the sole criterion for spontaneous change from the second law of thermodynamics? Starting with the definition

[redacted]

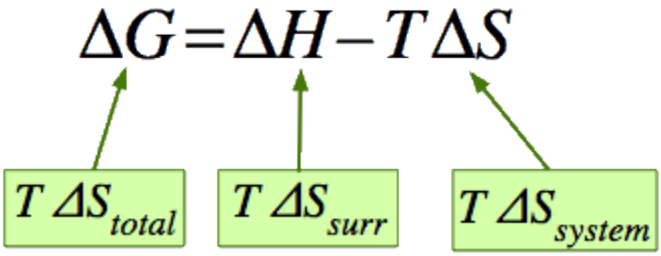
we would first like to get rid of ΔS_{surr}. How can a chemical reaction (a change in the *system*) affect the entropy of the *surroundings*? Because most reactions are either exothermic or endothermic, they are accompanied by a flow of heat q_p across the system boundary. The enthalpy change of the reaction ΔH is defined as the flow of heat into the system from the surroundings when the reaction is carried out at constant pressure, so the heat withdrawn from the surroundings will be $-q_p$ which will cause the entropy of the surroundings to change by $-q_p/T = -\Delta H/T$. We can therefore rewrite Equation 2.8.1021 as

[redacted]

Multiplying each side by $-T$, we obtain

[redacted]

which expresses the entropy change of the world in terms of thermodynamic properties of the *system* exclusively. If $-T\Delta S_{total}$ is denoted by ΔG, then we have Equation 2.8.1020 which defines the *Gibbs energy* change for the process.



From the foregoing, you should convince yourself that G will decrease in any process occurring at constant temperature and pressure which is accompanied by an overall increase in the entropy. The constant temperature is a consequence of the temperature and the enthalpy appearing in the preceding Equation 2.8.1024. Since most chemical and phase changes of interest to chemists take place under such conditions, the Gibbs energy is the most useful of all the thermodynamic properties of a substance, and (as we shall see in the lesson that follows this one) it is closely linked to the equilibrium constant.

Some textbooks and teachers say that the free energy, and thus the spontaneity of a reaction, depends on both the enthalpy and entropy changes of a reaction, and they sometimes even refer to reactions as "energy driven" or "entropy driven" depending on whether ΔH or the $T\Delta S$ term dominates. This is technically correct, but misleading because it disguises the important fact that ΔS_{total}, which this equation expresses in an indirect way, is the *only* criterion of spontaneous change.

Helmholtz Energy is also a "Free Energy"

We will deal only with the Gibbs energy in this course. The Helmholtz free energy is of interest mainly to chemical engineers (whose industrial-scale processes are often confined to tanks and reactors of fixed volume) and some geochemists whose interest is centered on the chemistry that occurs deep within the earth's surface.

Gibbs Energy and Chemical Change

Remember that ΔG is meaningful only for changes in which the *temperature and pressure remain constant*. These are the conditions under which most reactions are carried out in the laboratory; the system is usually open to the atmosphere (constant pressure) and we begin and end the process at room temperature (after any heat we have added or which is liberated by the reaction has dissipated.) The importance of the Gibbs function can hardly be over-stated: it serves as the single master variable that determines whether a given chemical change is thermodynamically possible. Thus if the free energy of the reactants is greater than that of the products, the entropy of the world will increase when the reaction takes place as written, and so the reaction will tend to take place spontaneously. Conversely, if the free energy of the products exceeds that of the reactants, then the reaction will not take place in the direction written, but it will tend to proceed in the reverse direction.

> ΔG serves as the single master variable that determines whether a given chemical change is thermodynamically possible. Moreover, it determines the direction and extent of chemical change.

In a spontaneous change, Gibbs energy always decreases and never increases. This of course reflects the fact that the entropy of the world behaves in the exact opposite way (owing to the negative sign in the $T\Delta S$ term).

[redacted]

water below its freezing point undergoes a decrease in its entropy, but the heat released into the surroundings more than compensates for this, so the entropy of the world increases, the free energy of the H_2O diminishes, and the process proceeds spontaneously.

> In a spontaneous change, Gibbs energy **always** decreases and never increases.

An important consequence of the one-way downward path of the free energy is that once it reaches its minimum possible value, all

net change comes to a halt. This, of course, represents the state of chemical equilibrium. These relations are nicely summarized as follows:

- $\Delta G < 0$: reaction can spontaneously proceed to the right:

$$A \rightarrow B$$

- $\Delta G > 0$: reaction can spontaneously proceed to the left:

$$A \leftarrow B$$

- $\Delta G = 0$: the reaction is at **equilibrium** and both $[A]$ and $[B]$ will not change:

$$A \rightleftharpoons B.$$

No need to find the value of ΔG for a Specific Reaction!

This might seem strange, given the key importance ΔG in determining whether or not a reaction will take place in a given direction. It turns out, however, that it is almost never necessary to explicitly evaluate ΔG. As we will show in the lesson that follows this one, it is far more convenient to work with the equilibrium constant of a reaction, within which ΔG is "hidden". This is just as well, because for most reactions (those that take place in solutions or gas mixtures) the value of ΔG depends on the **proportions** of the various reaction components in the mixture; it is not a simple sum of the "products minus reactants" type, as is the case with ΔH.

Recalling the condition for spontaneous change

$$\Delta G = \Delta H – T\Delta S < 0 \tag{5.3.1583}$$

it is apparent that the temperature dependence of ΔG depends almost entirely on the entropy change associated with the process. (We say "almost" because the values of ΔH and ΔS are themselves slightly temperature dependent; both gradually increase with temperature). In particular, notice that in the above equation **the sign of the entropy change determines whether the reaction becomes more or less spontaneous as the temperature is raised.** For any given reaction, the sign of ΔH can also be positive or negative. This means that there are four possibilities for the influence that temperature can have on the spontaneity of a process:

Case 1: ΔH < 0 and ΔS > 0

Both enthalpic ΔH and entropic $-T\Delta S$ terms will be negative, so ΔG will be negative regardless of the temperature. An exothermic reaction whose entropy increases will be spontaneous at all temperatures.

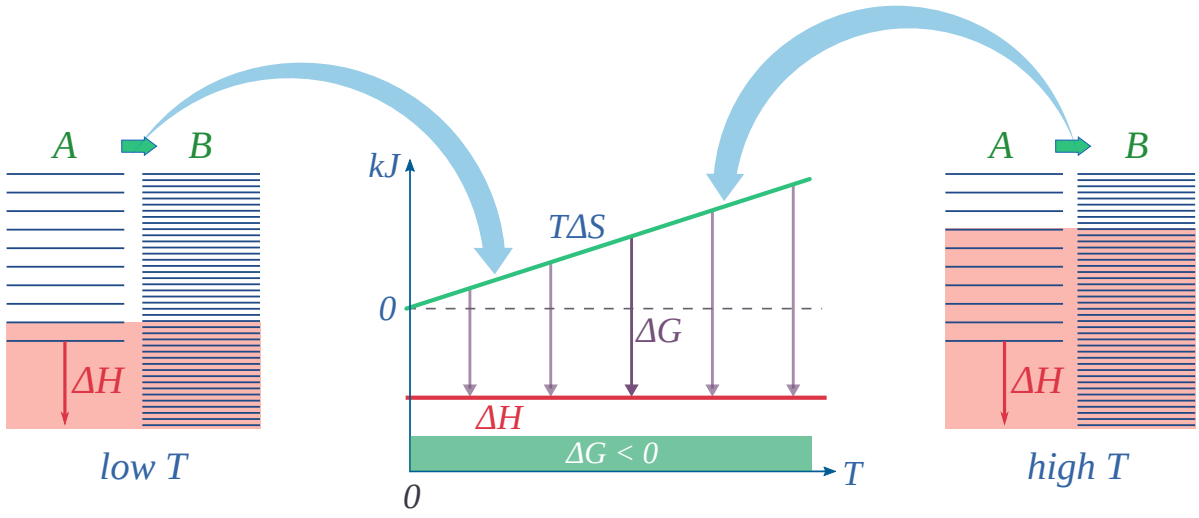


Figure 5.3.1: A hypothetical $\mathrm{A} \longrightarrow \mathrm{B}$ reaction that is favored enthalpically and entropically (spontaneous at all temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

Case 2: ΔH < 0 and ΔS < 0

If the reaction is sufficiently exothermic it can force ΔG negative only at temperatures below which $|T\Delta S| < |\Delta H|$. This means that there is a temperature $T = \Delta H/\Delta S$ at which the reaction is at equilibrium; the reaction will only proceed spontaneously below this temperature. The freezing of a liquid or the condensation of a gas are the most common examples of this condition.

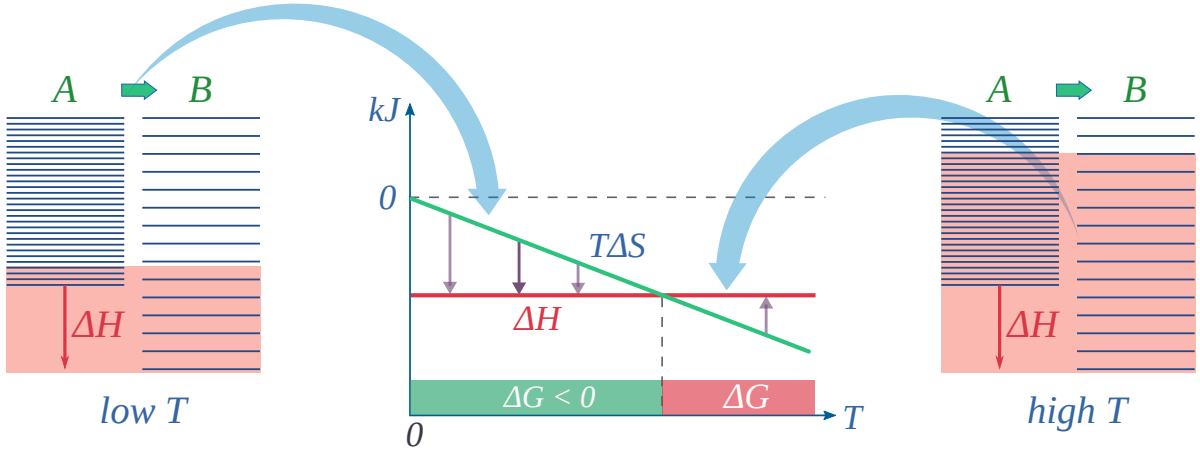


Figure 5.3.2: A hypothetical $\mathrm{A} \longrightarrow \mathrm{B}$ reaction that is favored enthalpically and is not favored entropically (spontaneous at low temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

Case 3: ΔH > 0 and ΔS > 0

This is the reverse of the previous case; the entropy increase must overcome the handicap of an endothermic process so that $T\Delta S > \Delta H$. Since the effect of the temperature is to "magnify" the influence of a positive ΔS, the process will be spontaneous at temperatures above $T = \Delta H/\Delta S$. (Think of melting and boiling.)

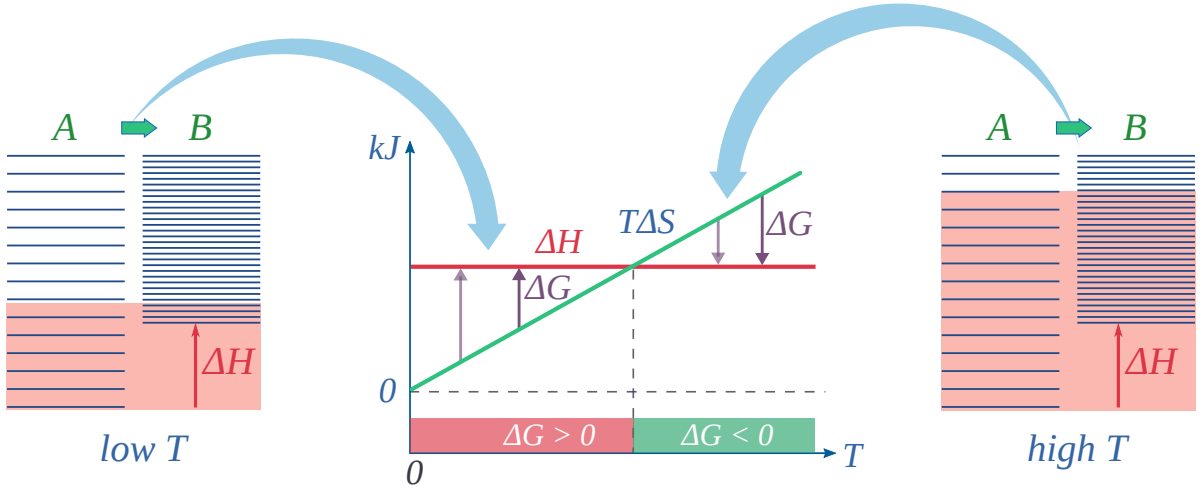


Figure 5.3.3: A hypothetical $\mathrm{A} \longrightarrow \mathrm{B}$ reaction that is not favored enthalpically and is favored entropically (spontaneous at high temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

Case 4: Δ*H* > 0 and Δ*S* < 0

With both ΔH and ΔS working against it, this kind of process will not proceed spontaneously at any temperature. Substance A always has a greater number of accessible energy states, and is therefore always the preferred form.

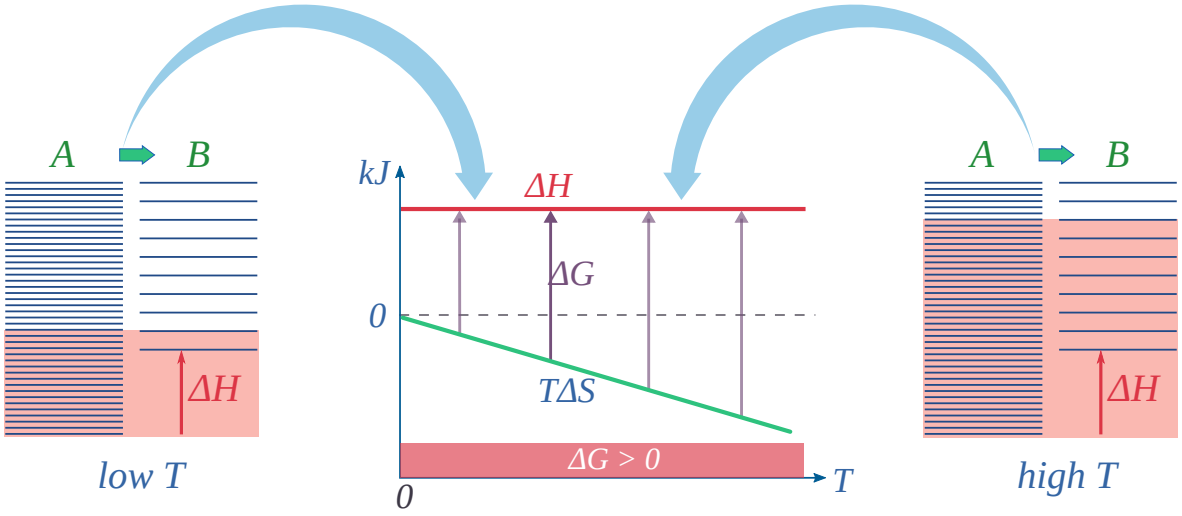


Figure 5.3.4: A hypothetical $\mathrm{A} \longrightarrow \mathrm{B}$ reaction that is not favored enthalpically and is not is favored entropically (not spontaneous at temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

The plots above are the important ones; do not try to memorize them, but make sure you understand and can explain or reproduce them for a given set of Δ*H* and Δ*S*.

- Their most important differentiating features are the position of the Δ*H* line (above or below the is *T*Δ*S* line), and the slope of the latter, which of course depends on the sign of Δ*S*.
- The reaction A → B will occur spontaneously only when Δ*G* is negative (blue arrows pointing down.)
- *T*Δ*S* plots are not quite straight lines as shown here. Similarly, the lines representing Δ*H* are even more curved.

The other two plots on each diagram are only for the chemistry-committed.

- Each pair of energy-level diagrams depicts the relative spacing of the microscopic energy levels in the reactants and products as reflected by the value of Δ*S*°. (The greater the entropy, the more closely-spaced are the quantized microstates.)
- The red shading indicates the range of energy levels that are accessible to the system at each temperature. The spontaneous direction of the reaction will always be in the direction in which the red shading overlaps the greater number of energy levels, resulting in the maximum dispersal of thermal energy.
- Note that the vertical offsets correspond to Δ*H*° for the reaction.
- Never forget that it is the ability of thermal energy to spread into as many of these states as possible that determines the tendency of the process to take place. None of this is to scale, of course!

The Standard Gibbs Energy

You have already been introduced to the terms such as ΔU^o and ΔH^o in which the ^{o} sign indicates that all components (reactants and products) are in their *standard states*. This concept of standard states is especially important in the case of the free energy, so let's take a few moments to review it. More exact definitions of the conventional standard states can be found in most physical chemistry textbooks. In specialized fields such as biochemistry and oceanography, alternative definitions may apply. For example, the "standard pH" of zero (corresponding to $[H^+] = 1\ M$) is impractical in biochemistry, so pH = 7 is commonly employed. For most practical purposes, the following definitions are good enough:

- **gases:** 1 atmosphere partial pressure
- **pure liquids:** the liquid under a total (hydrostatic) pressure of 1 atm.
- **solutes:** an effective concentration of 1 mol L^{-1} (1 mol dm^{-3}). ("Effective" concentrations approach real concentrations as the

latter approach zero; for practical purposes, these can be considered identical at real concentrations smaller than about 10^{-4} molar.)
- **solids:** the pure solid under 1 atm pressure

Reminder on Standard States

- There is actually no "standard temperature", but because most thermodynamics tables list values for 298.15 K (25° C), this temperature is usually implied.
- These same definitions apply to standard enthalpies and internal energies.
- Do not confuse these thermodynamic standard states with the "standard temperature and pressure" (STP) widely employed in gas law calculations.

To make use of Gibbs energies to predict chemical changes, we need to know the free energies of the individual components of the reaction. For this purpose we can combine the standard enthalpy of formation and the standard entropy of a substance to get its **standard free energy of formation**

[redacted]

Recall that the symbol ° refers to the *standard state* of a substance measured under the conditions of 1 atm pressure or an effective concentration of 1 mol L^{-1} and a temperature of 298 K. Then determine the standard Gibbs energy of the reaction according to

[redacted]

As with standard heats of formation, the standard free energy of a substance represents the free energy change associated with the formation of the substance from the elements in their most stable forms as they exist under the standard conditions of 1 atm pressure and 298 K. Standard Gibbs free energies of formation are normally found directly from tables. Once the values for all the reactants and products are known, the standard Gibbs energy change for the reaction is found by Equation 5.3.1154. Most tables of thermodynamic values list ΔG_f^o values for common substances (e.g., Table T2), which can, of course, always be found from values of $\Delta H_f°$ and $\Delta S_f°$.

Example 5.3.1

Find the standard Gibbs energy change for the reaction

$$\mathrm{CaCO_3\,(s)} \rightarrow \mathrm{CaO\,(s) + CO_2\,(g)}$$

The ΔG_f^o ° values for the three components of this reaction system are $\mathrm{CaCO_3\,(s)}$: –1128 kJ mol^{-1}, CaO*(s)*: –603.5 kJ mol^{-1}, CO_2*(g)*: –137.2 kJ mol^{-1}.

Solution

Substituting into Equation 5.3.1154, we have

$$\Delta G^o = (–603.5–137.2)–(–1128) kJ\,mol^{-1} = +130.9\,kJ\,mol^{-1}$$

This indicates that the process is not spontaneous under standard conditions (i.e., solid calcium carbone will not form solid calcium oxide and CO_2 at 1 atm partial pressure at 25° C).

Comment: This reaction is carried out on a huge scale to manufacture cement, so it is obvious that the process can be spontaneous under different conditions.

The practical importance of the Gibbs energy is that it allows us to make predictions based on the properties ($\Delta G°$ values) of

the reactants and products themselves, eliminating the need to experiment. But bear in mind that while thermodynamics always correctly predicts whether a given process *can* take place (is spontaneous in the thermodynamic sense), it is unable to tell us if it *will* take place at an observable rate.

When thermodynamics says "no", it means exactly that. When it says "yes", it means "maybe".

Example 5.3.2

The reaction

$$\tfrac{1}{2}\,\mathrm{O_2\,(g)} + \mathrm{H_2\,(g)} \longrightarrow \mathrm{H_2O\,(l)}$$

is used in fuel cells to produce an electrical current. The reaction can also be carried out by direct combustion.

Thermodynamic data: molar entropies in J mol^{-1} K^{-1}: O_2(g) 205.0; H_2(g)130.6; H_2O(l) 70.0; H_2O(l) $\Delta H°_f$ = –285.9 kJ mol^{-1}.

Use this information to find

a. The amount of heat released when the reaction takes place by direct combustion;
b. The amount of electrical work the same reaction can perform when carried out in a fuel cell at 298 K under reversible conditions;
c. The amount of heat released under the same conditions.

Solution

First, we need to find ΔH^o and ΔS^o for the process. Recalling that the standard enthalpy of formation of the elements is zero,

$$\begin{aligned}\Delta H^o &= \Delta H^p_f(\text{products}) – \Delta H^\circ_f(\text{reactants}) \\ &= –285.9\,kJ\,mol^{-1} – 0 \\ &= –285.9\,kJ\,mol^{-1}\end{aligned}\quad .$$

Similarly,

$$\begin{aligned}\Delta S^o &= S^o_f(\text{products}) – S^o_f(\text{reactants}) \\ &= (70.0) – (½ \times 205.0 + 130.6) \\ &= –163\,J\,K^{-1}mol^{-1}\end{aligned}$$

a. When the hydrogen and oxygen are combined directly, the heat released will be $\Delta H^o = –285.9\ kJ\ mol^{-1}$.
b. The maximum electrical work the fuel cell can perform is given by

$$\begin{aligned}\Delta G^o &= \Delta H^o – T\Delta S^o \\ &= –285.9\,kJ\,mol^{-1} – (298\,K)(–163\,JK^{-1}mol^{-1}). \\ &= –237.2\,kJ\,mol^{-1}.\end{aligned}$$

c. The heat released in the fuel cell reaction is the difference between the enthalpy change (the total energy available) and the reversible work that was expended:

$$\begin{aligned}\Delta H^o – \Delta G^o &= T\Delta S^o \\ &= (298\,K)(–163\,JK^{-1}mol^{-1}) \\ &= –48,800\,J\,mol^{-1} \\ &= –48.8\,kJ\,mol^{-1}.\end{aligned}\quad .$$

The foregoing example illustrates an important advantage of fuel cells. Although direct combustion of a mole of hydrogen gas yields more energy than is produced by the same net reaction within the fuel cell, the latter, in the form of electrical energy, can be utilized at nearly 100-percent energy efficiency by a motor or some other electrical device. If the thermal energy released by direct combustion were supplied to a heat engine, second-law considerations would require that at least half of this energy be "wasted" to the surroundings.

ΔG vs. ΔG°: what's the difference?

ΔG° refer to *single, specific chemical changes* in which all components (reactants and products) are in their *standard states*.

The ΔG_f^o of a substance, like ΔH_f^o, refers to the reaction in which that substance is formed from the elements as they exist in their most stable forms at 1 atm pressure and (usually) 298 K. Both of these terms are by definition zero for the elements in their standard states. There are only a few common cases in which this might create some ambiguity:

Table 5.3.1*: Standard Gibbs Energies of Select Substances*

Stable Form	ΔG_f^o (kJ mol^{-1})	Unstable Form	ΔG_f^o (kJ mol^{-1})
$O_2\,(g)$	0	$O_3\,(g)$	163.2
$C(\text{graphite})$	0	$C(\text{diamond})$	2.9
$S(\text{rhombic})$	0	$S(\text{monoclinic})$	0.1
$P(\text{white})$	0	$P_4\,(g)$	24.4

Ions in aqueous solution are a special case; their standard free energies are relative to the hydrated hydrogen ion $H^+\,(aq)$ which is assigned $\Delta G_f^o = 0$.

ΔG is very different from ΔG°. The distinction is nicely illustrated in Figure 5.3.5 in which ΔG is plotted on a vertical axis for two hypothetical reactions having opposite signs of ΔG°. The horizontal axis schematically expresses the relative concentrations of reactants and products at any point of the process. Note that the origin corresponds to the composition at which half of the reactants have been converted into products.

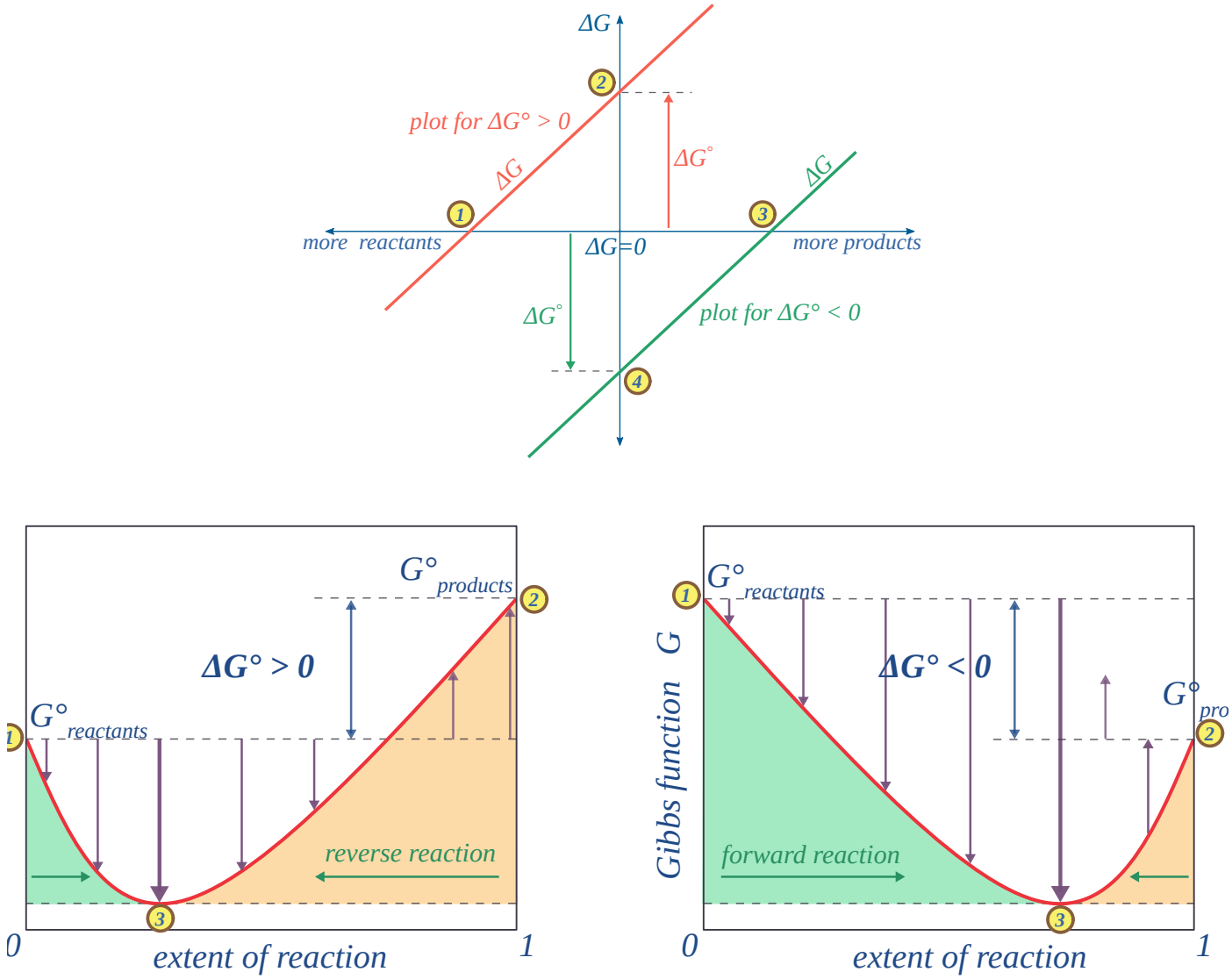


Figure 5.3.5: (CC BY 4.0; Ümit Kaya via LibreTexts)

Take careful note of the following:

- for the $\Delta G° > 0$ reaction. Notice that there are an infinite number of these values, depending on the progress of the reaction. In contrast there is only a single value (2) of $\Delta G°$, corresponding to the composition at which $\Delta G = 0$ (1).
- At this point, some products have been formed, but the composition is still dominated by reactants.
- If we begin at a composition to the left of (1), ΔG will be negative and the composition will move to the right. Similarly if we begin with a composition to the right of (1), ΔG will be positive and the composition will move to the left.
- The plot on the right is for the $\Delta G° < 0$ reaction, for which $\Delta G°$ is shown at (4). At its equilibrium point (3), there are more products than reactants. If we start at a composition to the right of (3), the composition will tend to move to the left. If the initial composition is to the left of (3), the reaction will tend to proceed to the right.
- What would happen if $\Delta G°$ were 0? The equilibrium point of such a reaction would be at the origin, corresponding to half the reactants being converted to products.

The important principle you should understand from this is that a negative $\Delta G°$ does not mean that the reactants will be completely transformed into products. By the same token, a positive $\Delta G°$ does not mean that no products are formed at all.

It should now be clear from the discussion above that a given reaction carried out under standard conditions is characterized by a *single value* of $\Delta G°$.

The reason for the Gibbs energy minimum at equilibrium relates to the increase in entropy when products and reactants coexist in the same phase. As seen in the plot, even a minute amount of "contamination" of products by reactants reduces the free energy below that of the pure products. In contrast, composition of a chemical reaction system undergoes continual change until the equilibrium state is reached. So the a single reaction can have an infinite number of ΔG values, reflecting the infinite possible compositions between the extremes of pure reactants (zero extent of reaction) and pure products (unity extent of reaction).

In the example of a reaction A → B, depicted in the above diagram, the standard free energy of the products (2) is smaller than that of the reactants (1), so the reaction will take place spontaneously. This does not mean that each mole of pure A will be converted into one mole of pure B. For reactions in which products and reactants occupy a single phase (gas or solution), the meaning of "spontaneous" is that the equilibrium composition (3) will correspond to an extent of reaction greater than 0.5 but smaller than unity.Note, however, that for $\Delta G°$ values in excess of about ±50 kJ mol^{-1}, the equilibrium composition will be negligibly different from zero or unity extent-of-reaction. The physical meaning of ΔG is that it tells us how far the free energy of the system has changed from $G°$ of the pure reactants (1). As the reaction proceeds to the right, the composition changes, and ΔG begins to fall. When the composition reaches (3), ΔG reaches its minimum value and further reaction would cause it to rise. But because free energy can only decrease but never increase, this does not happen. The composition of the system remains permanently at its equilibrium value.

A *G vs.* extent-of-reaction diagram for a non-spontaneous reaction can be interpreted in a similar way; the equilibrium composition (3) will correspond to an extent of reaction greater than zero but less than 0.5. In this case, the minimum at (3) reflects the increase in entropy when the reactants are "contaminated" by a small quantity of products.

If all this detail about ΔG seems a bit overwhelming, do not worry: it all gets hidden in the equilibrium constant and reaction quotient that we discuss in the next lesson!

Interpretation of Standard Gibbs energy changes

Although it is ΔG rather than ΔG^o that serves as a criterion for spontaneous change at constant temperature and pressure, ΔG^o values are so readily available that they are often used to get a rough idea of whether a given chemical change is possible. This is practical to do in some cases, but not in others:

Example

It generally works for reactions such as

$$4\,\mathrm{NH_3\,(g)} + 5\,\mathrm{O_2\,(g)} \longrightarrow 4\,\mathrm{NO\,(g)} + 6\,\mathrm{H_2O\,(g)}$$

with $\Delta G^o = -1,010\ kJ$.

(industrially important for the manufacture of nitric acid) because ΔG^o is so negative that the reaction will be spontaneous and virtually complete under just about any reasonable set of conditions.

Example

The following reaction expresses the fact that the water molecule is thermodynamically stable:

$$2\,H_2\,(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow H_2O\,(l)$$

with $\Delta G^o = -237.2\ kJ$.

Note that this refers to *liquid* water (the standard state of H_2O at 25°). If you think about it, a negative standard Gibbs energy of formation (of which this is an example) can in fact be considered a definition of molecular stability.

Example

Similarly, dissociation of dihydrogen into its atoms is highly unlikely under standard conditions:

$$H_2O\,(g) \longrightarrow 2\,H\,(g) + O\,(g)$$

with $\Delta G^o = +406.6\ kJ$.

Again, an analogous situation would apply to any stable molecule.

Example

Now consider the dissociation of dinitrogen tetroxide

$$N_2O_4\,(g) \longrightarrow 2\,NO_2\,(g)$$

with $\Delta G^o = +2.8kJ$.

in which the positive value of $\Delta G°$ tells us that N_2O_4 at 1 atm pressure will not change into two moles of NO_2 at the same pressure, but owing to the small absolute value of $\Delta G°$, we can expect the spontaneity of the process to be quite sensitive to both the temperature (as shown in the table below) and to the pressure in exactly the way the Le Chatelier principle predicts.

Example

For reactions involving dissolved ions, one has to be quite careful. Thus for the dissociation of the weak hydrofluoric acid

$$HF\,(aq) \longrightarrow H^+\,(aq) + F^-\,(aq)$$

with $\Delta G^o = -317\ kJ$.

it is clear that a 1 mol/L solution of HF will not dissociate into 1M ions, but this fact is not very useful because if the HF is added to water, the initial concentration of the fluoride ion will be zero (and that of H^+ very close to zero), and the Le Chatelier principle again predicts that *some* dissociation will be spontaneous.

Example

It is common knowledge that dissociation of water into hydrogen- and hydroxyl ions occurs only very sparingly:

$$H_2O\,(l) \longrightarrow H^+\,(aq) + OH^-\,(aq)$$

with $\Delta G^o = 79.9\ kJ$.

which correctly predicts that the water will not form 1M (effective concentration) of the ions, but this is hardly news if you already know that the product of these ion concentrations can never exceed 10^{-14} at 298K.

Example

Finally, consider this most familiar of all phase change processes, the vaporization of liquid water:

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

with $\Delta G^o = 8.58\ kJ$.

Conversion of liquid water to its vapor at 1 atm partial pressure does not take place at 25° C, at which temperature the equilibrium partial pressure of the vapor (the "vapor pressure") is only 0.031 atm (23.8 torr.) Gaseous H_2O at a pressure of 1 atm can only exist at 100° C. Of course, water left in an open container at room temperature will spontaneously evaporate if the partial pressure of water vapor in the air is less than 0.031 atm, corresponding to a relative humidity of under 100%

Finding the Equilibrium Temperature

A reaction is in its equilibrium state when

[redacted]

The temperature at which this occurs is given by

[redacted]

If we approximate ΔH by ΔH^o and ΔS by ΔS^o, so Equation 5.3.1156 would be

[redacted]

We can then estimate the normal boiling point of a liquid. From the following thermodynamic data for water:

$H_2O(l)$	→	$H_2O(g)$	
–285.9		–241.8	$\Delta H°$ = +44.1 kJ
69.9		188.7	$\Delta S°$ = +118.7 J K^{-1}

Caution!

Because ΔH° values are normally expressed in kilojoules while ΔS° is given in joules, a very common student error is to overlook the need to express both in the same units.

We find that liquid water is in equilibrium with water vapor at a partial pressure of 1 atm when the temperature is

$$T = \frac{44,100\ J}{118.7\ J\ K^{-1}} = 371.5\ K \tag{5.3.1584}$$

But "*the normal boiling point of water is 373 K*", you say? Very true. The reason we are off here is that both $\Delta H°$ and $\Delta S°$ have their own temperature dependencies; we are using the "standard" 25° values without correcting them to 100° C. Nevertheless,

if you think about it, the fact that we can estimate the boiling point of a liquid from a table of thermodynamic data should be rather impressive! Of course, the farther one gets from 298 K, the more unreliable will be the result. Thus for the dissociation of dihydrogen into its atoms,

$$\begin{array}{lll} H_2(g) & \rightarrow & 2\ H(g) \\ 0 & & 2 \times (218.0) \qquad \Delta H^\circ = +436.0\ kJ \\ 130.6 & & 2 \times (114.6) \qquad \Delta S^\circ = +98.6\ J\ K^{-1} \end{array}$$

$$T = \frac{436,000\ J}{98.6\ JK^{-1}} = 4,420\ K \quad (5.3.1585)$$

All one can say here is that H_2 will break down at something over 3000 K or so. (You may already know that *all* molecules will dissociate into their atoms at high temperatures.) We tend to think of high temperatures as somehow "forcing" molecules to dissociate into their atoms, but this is wrong. In order to get the H–H bond to vibrate so violently through purely thermal excitation that the atoms would fly apart, a temperature more like 30,000 K would be required. The proper interpretation is at the temperature corresponding to $\Delta H/T\Delta S$, the molecule *spontaneously* absorbs energy from the surroundings sufficient to overcome the H-H bond strength.

Predicting the Effects of Temperature

The $T\Delta S$ term interacts with the ΔH term in ΔG to determine whether the reaction can take place at a given temperature. This can be more clearly understood by examining plots of $T\Delta S^o$ and ΔH^o as functions of the temperature for some actual reactions. Of course these parameters refer to standard states that generally do not correspond to the temperatures, pressures, or concentrations that might be of interest in an actual case. Nevertheless, these quantities are easily found and they can usefully predict the way that temperature affects these systems.

Case 1: Exothermic reaction, ΔS° > 0

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

- $\Delta H^o = -393\ kJ$
- $\Delta G^o = -394\ kJ$ at $298\ K$

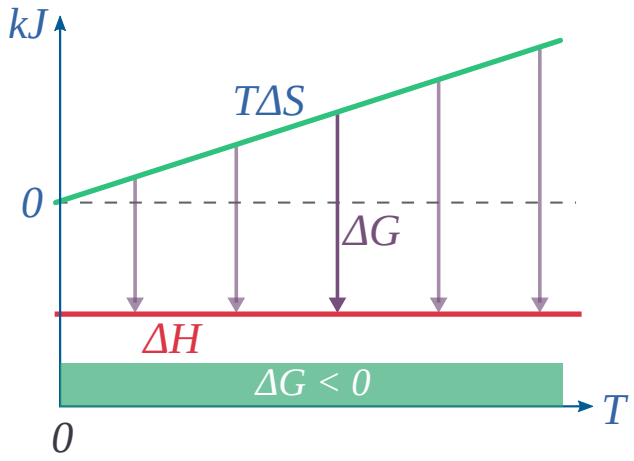


Figure 5.3.6: (CC BY 4.0; Ümit Kaya via LibreTexts)

This *combustion reaction*, like most such reactions, is **spontaneous at all temperatures**. The positive entropy change is due mainly to the greater mass of CO_2 molecules compared to those of O_2.

Case 2: Exothermic reaction, ΔS° < 0

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

- $\Delta H^o = -46.2\ kJ$
- $\Delta G^o = -16.4\ kJ$ at $298\ K$

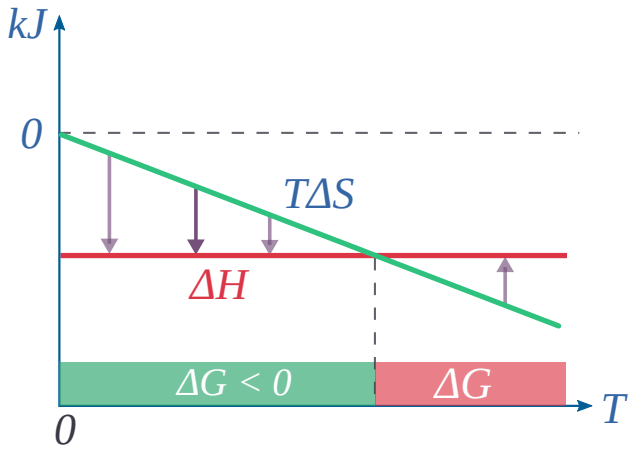


Figure 5.3.7: (CC BY 4.0; Ümit Kaya via LibreTexts)

The decrease in moles of gas in the **Haber ammonia synthesis** drives the entropy change negative, making the reaction **spontaneous only at low temperatures**. Thus higher T, which speeds up the reaction, also reduces its extent.

Case 3: Endothermic reaction, ΔS° > 0

$$N_2O_4\,(g) \longrightarrow 2\,NO_2\,(g)$$

- $\Delta H^o = 55.3\ kJ$
- $\Delta G^o = +2.8\ kJ$ at $298\ K$

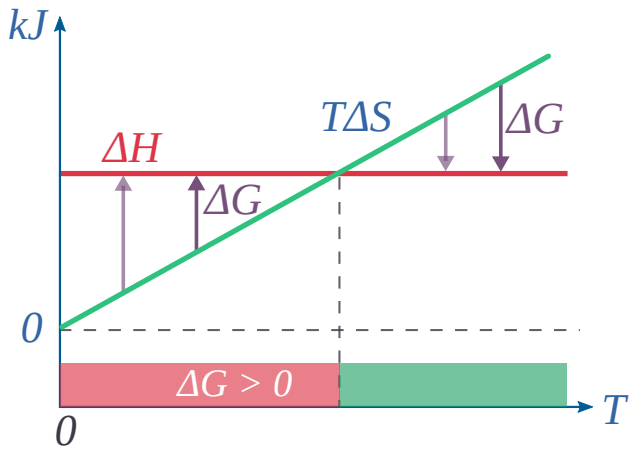


Figure 5.3.8: (CC BY 4.0; Ümit Kaya via LibreTexts)

Dissociation reactions are typically endothermic with positive entropy change, and are therefore **spontaneous at high temperatures**. Ultimately, all molecules decompose to their atoms at sufficiently high temperatures.

Case 4: Endothermic Reaction, ΔS° < 0

$$\tfrac{1}{2}\,\mathrm{N_2\,(g)} + \mathrm{O_2\ (g)} \longrightarrow \mathrm{NO_2\,(g)}$$

- $\Delta H^\circ = 33.2\ kJ$
- $\Delta S^o = -249\ J\ K^{-1}$
- $\Delta G^o = +51.3\ kJ$ at $298\ K$

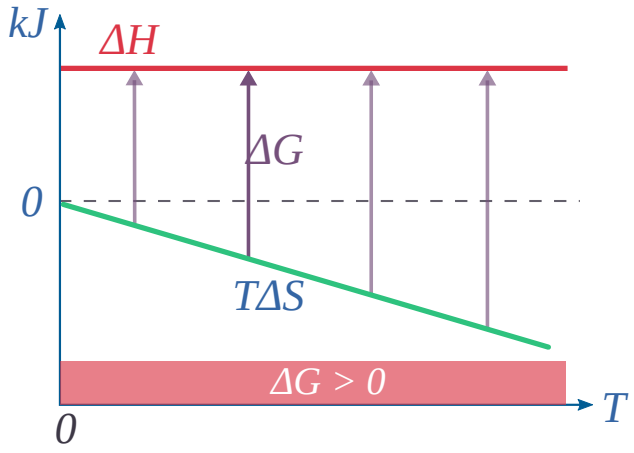


Figure 5.3.9: (CC BY 4.0; Ümit Kaya via LibreTexts)

This reaction is **not spontaneous at any temperature**, meaning that *its reverse is always spontaneous*. But because the reverse reaction is kinetically inhibited, NO_2 can exist indefinitely at ordinary temperatures even though it is thermodynamically unstable.

Concluding remarks on Gibbs Energy

The appellation “free energy” for G has led to so much confusion that many scientists now refer to it simply as the *Gibbs energy*. The “free” part of the older name reflects the steam-engine origins of thermodynamics with its interest in converting heat into work: ΔG is the maximum amount of energy, which can be “freed” from the system to perform useful work. By "useful", we mean work other than that which is associated with the expansion of the system. This is most commonly in the form of electrical work (moving electric charge through a potential difference), but other forms of work (osmotic work, increase in surface area) are also possible.

A much more serious difficulty with the Gibbs function, particularly in the context of chemistry, is that although G has the *units* of energy (joules, or in its intensive form, J mol^{-1}), it lacks one of the most important attributes of energy in that it is not *conserved*. Thus, although the free energy always falls when a gas expands or a chemical reaction takes place spontaneously, there need be no compensating *increase* in energy anywhere else. Referring to G as an energy also reinforces the false but widespread notion that a fall in energy must accompany any change. But if we accept that energy is conserved, it is apparent that the only necessary condition for change (whether the dropping of a weight, expansion of a gas, or a chemical reaction) is the *redistribution* of energy. The quantity \(-ΔG\) associated with a process represents the quantity of energy that is “shared and spread”, which as we have already explained is the meaning of the increase in the entropy. The quotient $-\Delta G/T$ is in fact identical with ΔS_{total}, the entropy change of the world, whose increase is the primary criterion for any kind of change.

G differs from the thermodynamic quantities H and S in another significant way: it has no physical reality as a property of matter, whereas H and S can be related to the quantity and distribution of energy in a collection of molecules. The free energy is simply a useful construct that serves as a criterion for change and makes calculations easier.

What Gibbs Energy is not...

- Gibbs Energy is not free energy
- Gibbs Energy is not energy
- Gibbs Energy is not even "real"

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5.4: The Law of Mass Action for Related and Simultaneous Equilibria

Learning Objectives

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.

Relationship among Equilibrium Expressions

Chemists frequently need to know the equilibrium constant for a reaction that has not been previously studied. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated values for the other reactions.

To illustrate this procedure, let's consider the reaction of N_2 with O_2 to give NO_2. This reaction is an important source of the NO_2 that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps. In the first reaction (1), N_2 reacts with O_2 at the high temperatures inside an internal combustion engine to give NO. The released NO then reacts with additional O_2 to give NO_2 (2). The equilibrium constant for each reaction at 100°C is also given.

1. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \qquad K_1 = 2.0 \times 10^{-25}$
2. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_2 = 6.4 \times 10^{9}$

Summing reactions (1) and (2) gives the overall reaction of N_2 with O_2:

3. $N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_3 = ?$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2} \tag{5.4.1586}$$

What is the relationship between K_1, K_2, and K_3, all at 100°C? The expression for K_1 has $[NO]^2$ in the numerator, the expression for K_2 has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for K_3. Multiplying K_1 by K_2 and canceling the $[NO]^2$ terms,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}\,[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3 \tag{5.4.1587}$$

Thus the product of the equilibrium constant expressions for K_1 and K_2 is the same as the equilibrium constant expression for K_3:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^{9}) = 1.3 \times 10^{-15} \tag{5.4.1588}$$

The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions. In contrast, recall that according to Hess's Law, ΔH for the sum of two or more reactions is the sum of the ΔH values for the individual reactions.

Note

To determine K for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.

Example 5.4.6

The following reactions occur at 1200°C:

1. $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \qquad K_1 = 9.17 \times 10^{-2}$
2. $CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)} \qquad K_2 = 3.3 \times 10^4$

Calculate the equilibrium constant for the following reaction at the same temperature.

3. $CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \qquad K_3 = ?$

Given: two balanced equilibrium equations, values of K, and an equilibrium equation for the overall reaction

Asked for: equilibrium constant for the overall reaction

Strategy:

Arrange the equations so that their sum produces the overall equation. If an equation had to be reversed, invert the value of K for that equation. Calculate K for the overall equation by multiplying the equilibrium constants for the individual equations.

Solution:

The key to solving this problem is to recognize that reaction 3 is the sum of reactions 1 and 2:

$$CO_{(g)} + \cancel{3H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)} \tag{5.4.1589}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + \cancel{3H_{2(g)}} + H_{2(g)} \tag{5.4.1590}$$

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \tag{5.4.1591}$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^4) = 3.03 \times 10^3 \tag{5.4.1592}$$

Exercise 5.4.6

In the first of two steps in the industrial synthesis of sulfuric acid, elemental sulfur reacts with oxygen to produce sulfur dioxide. In the second step, sulfur dioxide reacts with additional oxygen to form sulfur trioxide. The reaction for each step is shown, as is the value of the corresponding equilibrium constant at 25°C. Calculate the equilibrium constant for the overall reaction at this same temperature.

1. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)} \qquad K_1 = 4.4 \times 10^{53}$
2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_2 = 2.6 \times 10^{12}$
3. $\frac{1}{8}S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_3 = ?$

Answer

$$K_3 = 1.1 \times 10^{66}$$

Summary

An equilibrium system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium. When a reaction can be expressed as the sum of two or more reactions, its equilibrium constant is equal to the product of the equilibrium constants for the individual reactions.

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5.5: Gas-Phase and Heterogeneous Reaction Equilibria

Learning Objectives

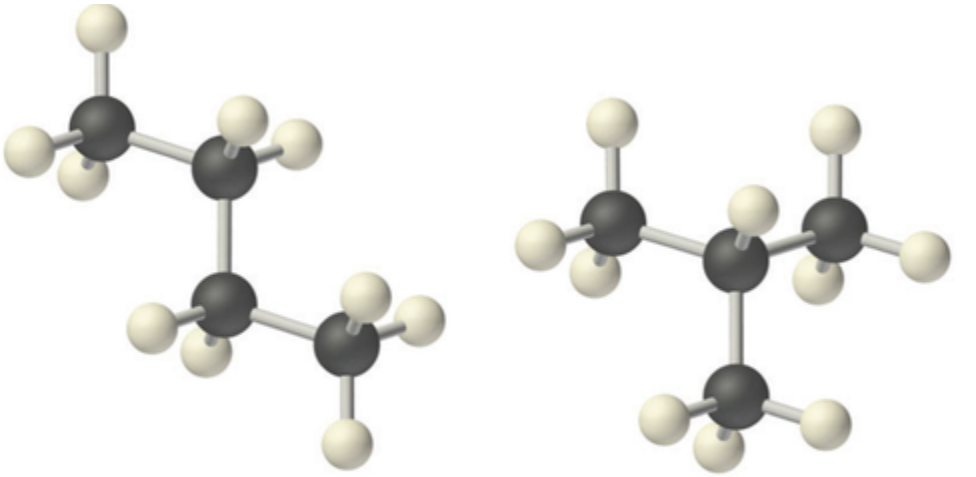
- To solve quantitative problems involving chemical equilibriums.

There are two fundamental kinds of equilibrium problems:

1. those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and
2. those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

Calculating an Equilibrium Constant from Equilibrium Concentrations

The equilibrium constant for the decomposition of $CaCO_{3(s)}$ to $CaO_{(s)}$ and $CO_{2(g)}$ is $K = [CO_2]$. At 800°C, the concentration of CO_2 in equilibrium with solid $CaCO_3$ and CaO is $2.5 \times 10^{-3}\ M$. Thus K at 800°C is 2.5×10^{-3} (remember that equilibrium constants are unitless). A more complex example of this type of problem is the conversion of n-butane, an additive used to increase the volatility of gasoline, into isobutane (2-methylpropane).



This reaction can be written as follows:

[redacted]

and the equilibrium constant $K = [\text{isobutane}]/[\text{n-butane}]$. At equilibrium, a mixture of n-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M n-butane. Substituting these concentrations into the equilibrium constant expression,

[redacted]

Thus the equilibrium constant for the reaction as written is 2.6.

Example 5.5.1

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:

$$2\,\mathrm{SO_2\,(g)} + \mathrm{O_2\,(g)} \rightleftharpoons 2\,\mathrm{SO_3\,(g)}$$

A mixture of SO_2 and O_2 was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained

- $5.0 \times 10^{-2}\ M\ SO_3$,
- $3.5 \times 10^{-3}\ M\ O_2$, and
- $3.0 \times 10^{-3}\ M\ SO_2$.

Calculate K and K_p at this temperature.

Given: balanced equilibrium equation and composition of equilibrium mixture

Asked for: equilibrium constant

Strategy

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain K.

Solution

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(5.0 \times 10^{-2})^2}{(3.0 \times 10^{-3})^2(3.5 \times 10^{-3})} = 7.9 \times 10^4$$

To solve for K_p, we need to identify Δn where $\Delta n = 2 - 3 = -1$ and then

$$K_p = K(RT)^{\Delta n}$$
$$K_p = 7.9 \times 10^4[(0.08206\ L \cdot atm/mol \cdot K)(800K)]^{-1}$$
$$K_p = 1.2 \times 10^3$$

Exercise 5.5.1

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$\mathrm{H_2\,(g)} + \mathrm{I_2\,(g)} \rightleftharpoons 2\,\mathrm{HI\,(g)}$$

A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained

- $1.37 \times 10^{-2}\ M\ HI$,
- $6.47 \times 10^{-3}\ M\ H_2$, and
- $5.94 \times 10^{-4}\ M\ I_2$.

Calculate K and K_p for this reaction.

Answer (K)

$$K = 48.8$$

Answer (K_p)

$$K_p = 48.8$$

Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example 5.5.2 shows one way to do this.

Example 5.5.2

A 1.00 mol sample of $NOCl$ was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl_2. Calculate K at this temperature. The equation for the decomposition of $NOCl$ to NO and Cl_2 is as follows:

$$2\,\mathrm{NOCl\,(g)} \rightleftharpoons 2\,\mathrm{NO\,(g)} + \mathrm{Cl_2\,(g)}$$

Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium

Asked for: K

Strategy:

A. Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).
B. Calculate all possible initial concentrations from the data given and insert them in the table.
C. Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.
D. Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

Solution

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of $NOCl$, NO, and Cl_2 at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial			
Change			
Final			

B Initially, the system contains 1.00 mol of $NOCl$ in a 2.00 L container. Thus $[NOCl]_i = 1.00\ mol/2.00\ L = 0.500\ M$. The initial concentrations of NO and Cl_2 are $0\ M$ because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f = 0.056\ mol/2.00\ L = 0.028\ M$. We insert these values into the following table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change			
Final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

$$\Delta[Cl_2] = 0.028\ M_{(final)} - 0.00\ M_{(initial)}] = +0.028\ M$$

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta[NO] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = 0.056\ M$$

Similarly, 2 mol of $NOCl$ are consumed for every 1 mol of Cl_2 produced, so the change in the $NOCl$ concentration is as follows:

$$\Delta[NOCl] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{-2\ mol\ NOCl}{1\ \cancel{mol\ Cl_2}}\right) = -0.056\ M$$

We insert these values into our table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change	−0.056	+0.056	+0.028
Final			0.028

D We sum the numbers in the $[NOCl]$ and $[NO]$ columns to obtain the final concentrations of NO and $NOCl$:

$$[NO]_f = 0.000\ M + 0.056\ M = 0.056\ M$$

$$[NOCl]_f = 0.500\ M + (-0.056\ M) = 0.444M$$

We can now complete the table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2(0.028)}{(0.444)^2} = 4.5 \times 10^{-4}$$

Exercise 5.5.2

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting $0.1248\ \ M\ \ H_2$ and $0.0416\ \ M\ \ N_2$ at about 500°C. At equilibrium, the mixture contained 0.00272 M NH_3. What is K for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

at this temperature? What is K_p?

Answer (K)

$$K = 0.105$$

Answer (K_p)

$$K_p = 2.61 \times 10^{-5}$$

Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of n-butane to isobutane (Equation 1.1.1), for which K = 2.6 at 25°C. If we begin with a 1.00 M sample of n-butane, we can determine the concentration of n-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example 5.5.2.

$$\text{n-butane}(g) \rightleftharpoons \text{isobutane}(g) \tag{5.5.1593}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial		
Change		
Final		

The initial concentrations of the reactant and product are both known: [n-butane]i = 1.00 M and [isobutane]i = 0 M. We need to calculate the equilibrium concentrations of both n-butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the change in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as +x, then the change in the concentration of n-butane is Δ[n-butane] = −x. This is because the balanced chemical equation for the reaction tells us that 1 mol of n-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{5.5.1594}$$

ICE	[n-butane$_{(g)}$]	[isobutane$_{(g)}$]
Initial	1.00	0
Change	−x	+x
Final	(1.00 − x)	(0 + x) = x

Substituting the expressions for the final concentrations of n-butane and isobutane from the table into the equilibrium equation,

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \frac{x}{1.00 - x} = 2.6 \tag{5.5.1595}$$

Rearranging and solving for x,

$$\begin{aligned} x &= 2.6(1.00 - x) = 2.6 - 2.6x \\ x + 2.6x &= 2.6 \\ x &= 0.72 \end{aligned}$$

We obtain the final concentrations by substituting this x value into the expressions for the final concentrations of n-butane and isobutane listed in the table:

$$[\text{n-butane}]_f = (1.00 - x)M = (1.00 - 0.72)M = 0.28\ M \tag{5.5.1596}$$

$$[\text{isobutane}]_f = (0.00 + x)M = (0.00 + 0.72)M = 0.72\ M \tag{5.5.1597}$$

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same K that we used in the calculation:

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \left(\frac{0.72\ \cancel{M}}{0.28\ \cancel{M}}\right) = 2.6 \tag{5.5.1598}$$

This is the same K we were given, so we can be confident of our results.

Example 5.5.3 illustrates a common type of equilibrium problem that you are likely to encounter.

Example 5.5.3

The water–gas shift reaction is important in several chemical processes, such as the production of H_2 for fuel cells. Thisreaction can be written as follows:

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

$K = 0.106$ at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?

Given: balanced equilibrium equation, K, and initial concentrations

Asked for: final concentrations

Strategy:

A. Construct a table showing what is known and what needs to be calculated. Define x as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of x. From the values in the table, calculate the final concentrations.

B. Write the equilibrium equation for the reaction. Substitute appropriate values from the ICE table to obtain x.
C. Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150\ \ M$. Just as before, we will focus on the change in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as x, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of x. For example, 1 mol of CO is produced for every 1 mol of H_2O, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
Initial	0.0150	0.0150	0	0
Change	–x	–x	+x	+x
Final	(0.0150 – x)	(0.0150 – x)	x	x

B We can now use the equilibrium equation and the given K to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(x)(x)}{(0.0150 - x)(0.0150 - x)} = \frac{x^2}{(0.0150 - x)^2} = 0.106$$

We could solve this equation with the quadratic formula, but it is far easier to solve for x by recognizing that the left side of the equation is a perfect square; that is,

$$\frac{x^2}{(0.0150 - x)^2} = \left(\frac{x}{0.0150 - x}\right)^2 = 0.106$$

Taking the square root of the middle and right terms,

$$\frac{x^2}{(0.0150 - x)^2} = (0.106)^{1/2} = 0.326$$

$$x = (0.326)(0.0150) - 0.326x$$

$$1.326x = 0.00489$$

$$x = 0.00369 = 3.69 \times 10^{-3}$$

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f = [H_2]_i + \Delta[H_2] = (0.0150 - 0.00369)\ \ M = 0.0113\ \ M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = (0.0150 - 0.00369)\ \ M = 0.0113\ \ M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = (0 + 0.00369)\ \ M = 0.00369\ \ M$
- $[CO]_f = [CO]_i + \Delta[CO] = (0 + 0.00369)\ \ M = 0.00369\ \ M$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

Exercise 5.5.3

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$K = 54$ at 425°C. If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer

$$[HI]_f = 0.270 \ M \ [H_2]_f = [I_2]_f = 0.037 \ M$$

In Example 5.5.3, the initial concentrations of the reactants were the same, which gave us an equation that was a perfect square and simplified our calculations. Often, however, the initial concentrations of the reactants are not the same, and/or one or more of the products may be present when the reaction starts. Under these conditions, there is usually no way to simplify the problem, and we must determine the equilibrium concentrations with other means. Such a case is described in Example 5.5.4.

Example 5.5.4

In the water–gas shift reaction shown in Example 5.5.3, a sample containing 0.632 M CO_2 and 0.570 M H_2 is allowed to equilibrate at 700 K. At this temperature, $K = 0.106$. What is the composition of the reaction mixture at equilibrium?

Given: balanced equilibrium equation, concentrations of reactants, and K

Asked for: composition of reaction mixture at equilibrium

Strategy:

A. Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations (x) and the final concentrations.
B. Write the equilibrium constant expression for the reaction. Substitute the known K value and the final concentrations to solve for x.
C. Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A $[CO_2]_i = 0.632 \ M$ and $[H_2]_i = 0.570 \ M$. Again, x is defined as the change in the concentration of H_2O: $\Delta[H_2O] = +x$. Because 1 mol of CO is produced for every 1 mol of H_2O, the change in the concentration of CO is the same as the change in the concentration of H2O, so Δ[CO] = +x. Similarly, because 1 mol each of H_2 and CO_2 are consumed for every 1 mol of H_2O produced, $\Delta[H_2] = \Delta[CO_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$H_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$	$CO_{(g)}$
Initial	0.570	0.632	0	0
Change	–x	–x	+x	+x
Final	(0.570 – x)	(0.632 – x)	x	x

B We can now use the equilibrium equation and the known K value to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106$$

In contrast to Example 5.5.3, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.20x + x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0$$

This equation can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)}$$

$$x = 0.148 \text{ and } -0.290$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O] = \Delta[CO] = +0.148M$, and $\Delta[H_2] = \Delta[CO_2] = -0.148\ M$.

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f[= [H_2]_i + \Delta[H_2] = 0.570\ M - 0.148\ M = 0.422M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = 0.632\ M - 0.148\ M = 0.484M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = 0\ M + 0.148\ M = 0.148\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = 0M + 0.148\ M = 0.148M$

We can check our work by substituting these values into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.148)^2}{(0.422)(0.484)} = 0.107$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

Exercise 5.5.4

The exercise in Example 5.5.1 showed the reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K = 54$ at 425°C. If a sample containing 0.200 M H_2 and 0.0450 M I_2 is allowed to equilibrate at 425°C, what is the final concentration of each substance in the reaction mixture?

Answer

$$[H_I]_f = 0.0882\ M$$

$$[H_2]_f = 0.156\ M$$

$$[I_2]_f = 9.2 \times 10^{-4} M$$

In many situations it is not necessary to solve a quadratic (or higher-order) equation. Most of these cases involve reactions for which the equilibrium constant is either very small ($K \leq 10^{-3}$) or very large ($K \geq 10^{3}$), which means that the change in the concentration (defined as x) is essentially negligible compared with the initial concentration of a substance. Knowing this simplifies the calculations dramatically, as illustrated in Example 5.5.5.

Example 5.5.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$\mathrm{N_2\,(g) + O_2\,(g)\ \rightleftharpoons\ 2\,NO\,(g)} \tag{5.5.1599}$$

with $K_p = 2.0 \times 10^{-31}$ at 25°C.

What is the partial pressure of NO in equilibrium with N_2 and O_2 in the atmosphere (at 1 atm) $P_{N_2} = 0.78\ \ atm$ and $P_{O_2} = 0.21\ \ atm$?

Given: balanced equilibrium equation and values of K_p, P_{O_2}, and P_{N_2}

Asked for: partial pressure of NO

Strategy:

A. Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.
B. Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration (x).
C. Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for K.

Solution

A Because we are given Kp and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of O_2 is 0.21 atm and that of N_2 is 0.78 atm. If we define the change in the partial pressure of NO as 2x, then the change in the partial pressure of O_2 and of N_2 is –x because 1 mol each of N_2 and of O_2 is consumed for every 2 mol of NO produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

$$\mathrm{N_2\,(g) + O_2\,(g)\ \rightleftharpoons\ 2\,NO\,(g)} \tag{5.5.1600}$$

ICE	P_{N_2}	P_{O_2}	P_{NO}
Initial	0.78	0.21	0
Change	–x	–x	+2x
Final	(0.78 – x)	(0.21 – x)	2x

B Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78 - x)(0.21 - x)} = 2.0 \times 10^{-31}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very

small; therefore, the x value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, (0.78 – x) = 0.78 and (0.21 – x) = 0.21. Substituting these expressions into our original equation,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4}$$

$$x^{=}9.1 \times 10^{-17}$$

C Substituting this value of x into our expressions for the final partial pressures of the substances,

- $P_{NO} = 2x \;\; atm = 1.8 \times 10^{-16} \;\; atm$
- $P_{N_2} = (0.78 - x) \;\; atm = 0.78 \;\; atm$
- $P_{O_2} = (0.21 - x) \;\; atm = 0.21 \;\; atm$

From these calculations, we see that our initial assumption regarding x was correct: given two significant figures, 2.0×10^{-16} is certainly negligible compared with 0.78 and 0.21. When can we make such an assumption? As a general rule, if x is less than about 5% of the total, or $10^{-3} > K > 10^{3}$, then the assumption is justified. Otherwise, we must use the quadratic formula or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of N_2 and O_2 to a substantial degree at 25°C. We can verify our results by substituting them into the original equilibrium equation:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

The final K_p agrees with the value given at the beginning of this example.

Exercise 5.5.5

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$3O_{2(g)} \rightleftharpoons 2O_{3(g)}$$

with $K_p = 2.5 \times 10^{-59}$ at 25°C. What ozone partial pressure is in equilibrium with oxygen in the atmosphere ($P_{O_2} = 0.21 \;\; atm$)?

Answer

$$4.8 \times 10^{-31} \;\; atm$$

Another type of problem that can be simplified by assuming that changes in concentration are negligible is one in which the equilibrium constant is very large (K ≥ 10^3). A large equilibrium constant implies that the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion. When we solve this type of problem, we view the system as equilibrating from the products side of the reaction rather than the reactants side. This approach is illustrated in Example 5.5.6.

Example 5.5.6

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

with $K = 9.6 \times 10^{18}$ at 25°C. If a mixture of 0.200 M H_2 and 0.155 M C_2H_4 is maintained at 25°C in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

Given: balanced chemical equation, K, and initial concentrations of reactants

Asked for: equilibrium concentrations

Strategy:

A. Construct a table showing initial concentrations, concentrations that would be present if the reaction were to go to completion, changes in concentrations, and final concentrations.
B. Write the equilibrium constant expression for the reaction. Then substitute values from the table into the expression to solve for x (the change in concentration).
C. Calculate the equilibrium concentrations. Check your answers by substituting these values into the equilibrium equation.

Solution:

A From the magnitude of the equilibrium constant, we see that the reaction goes essentially to completion. Because the initial concentration of ethylene (0.155 M) is less than the concentration of hydrogen (0.200 M), ethylene is the limiting reactant; that is, no more than 0.155 M ethane can be formed from 0.155 M ethylene. If the reaction were to go to completion, the concentration of ethane would be 0.155 M and the concentration of ethylene would be 0 M. Because the concentration of hydrogen is greater than what is needed for complete reaction, the concentration of unreacted hydrogen in the reaction mixture would be 0.200 M – 0.155 M = 0.045 M. The equilibrium constant for the forward reaction is very large, so the equilibrium constant for the reverse reaction must be very small. The problem then is identical to that in Example 5.5.5. If we define –x as the change in the ethane concentration for the reverse reaction, then the change in the ethylene and hydrogen concentrations is +x. The final equilibrium concentrations are the sums of the concentrations for the forward and reverse reactions.

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

IACE	$[H_{2(g)}]$	$[C_2H_{4(g)}]$	$[C_2H_{6(g)}]$
Initial	0.200	0.155	0
Assuming 100% reaction	0.045	0	0.155
Change	+x	+x	–x
Final	(0.045 + x)	(0 + x)	(0.155 – x)

B Substituting values into the equilibrium constant expression,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18}$$

Once again, the magnitude of the equilibrium constant tells us that the equilibrium will lie far to the right as written, so the reverse reaction is negligible. Thus x is likely to be very small compared with either 0.155 M or 0.045 M, and the equation can be simplified [(0.045 + x) = 0.045 and (0.155 – x) = 0.155] as follows:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18}$$

$$x = 3.6 \times 10^{-19}$$

C The small x value indicates that our assumption concerning the reverse reaction is correct, and we can therefore calculate the final concentrations by evaluating the expressions from the last line of the table:

- $[C_2H_6]_f = (0.155 - x)\ \ M = 0.155\ \ M$
- $[C_2H_4]_f = x\ \ M = 3.6 \times 10^{-19} M$
- $[H_2]_f = (0.045 + x)\ \ M = 0.045\ \ M$

We can verify our calculations by substituting the final concentrations into the equilibrium constant expression:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

This K value agrees with our initial value at the beginning of the example.

Exercise 5.5.6

Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

with $K_p = 4.0 \times 10^{31}$ at 47°C. If a mixture of 0.257 M H_2 and 0.392 M Cl_2 is allowed to equilibrate at 47°C, what is the equilibrium composition of the mixture?

Answer

$[H_2]_f = 4.8 \times 10^{-32}\ \ M$

$[Cl_2]_f = 0.135\ \ M$

$[HCl]_f = 0.514\ \ M$

Summary

Various methods can be used to solve the two fundamental types of equilibrium problems:

1. those in which we calculate the concentrations of reactants and products at equilibrium and
2. those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture.

When an equilibrium constant is calculated from equilibrium concentrations, molar concentrations or partial pressures are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

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5.6: The Direction of Change in Chemical Reactions: Empirical Description

Learning Objectives

- To predict in which direction a reaction will proceed.
- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

We previously saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

The Reaction Quotient

To determine whether a system has reached equilibrium, chemists use a quantity called the Reaction Quotient (Q). The expression for the Reaction Quotient has precisely the same form as the equilibrium constant expression from the Law of Mass Action, except that Q may be derived from a set of values measured at any time during the reaction of any mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:

$$aA + bB \rightarrow cC + dD \tag{5.6.1601}$$

the Reaction Quotient is defined as follows:

[redacted]

To understand how information is obtained using a Reaction Quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,

[redacted]

For this reaction, $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

[redacted]

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of Q were calculated for each. Each experiment begins with different proportions of product and reactant:

Table 5.6.1: Three Conditions of the dissociation of dinitrogen tetroxide to nitrogen dioxide (Equation 5.6.1)

Experiment	$[NO_2]\ (M)$	$[N_2O_4]\ (M)$	$Q = \frac{[NO^2]^2}{[N^2O^4]}$
1	0	0.0400	$\frac{0^2}{0.0400} = 0$
2	0.0600	0	$\frac{(0.0600)^2}{0} = \text{undefined}$
3	0.0200	0.0600	$\frac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$

As these calculations demonstrate, Q can have any numerical value between 0 and infinity (undefined); that is, Q can be greater than, less than, or equal to K.

Comparing the magnitudes of Q and K enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes Q approach K. If $Q = K$, for example, then the system is already at equilibrium, and no further change in the composition of the system will occur unless the conditions are changed. If $Q < K$, then the ratio of the concentrations of products to the concentrations of reactants is less than the ratio at equilibrium. Therefore, the reaction will proceed to the right as written, forming products at the expense of reactants. Conversely, if $Q > K$, then the ratio of the concentrations of products to the concentrations of reactants is greater than at equilibrium, so the reaction will proceed to the left as written, forming reactants at the expense of products. These points are illustrated graphically in Figure $5.6.1$.

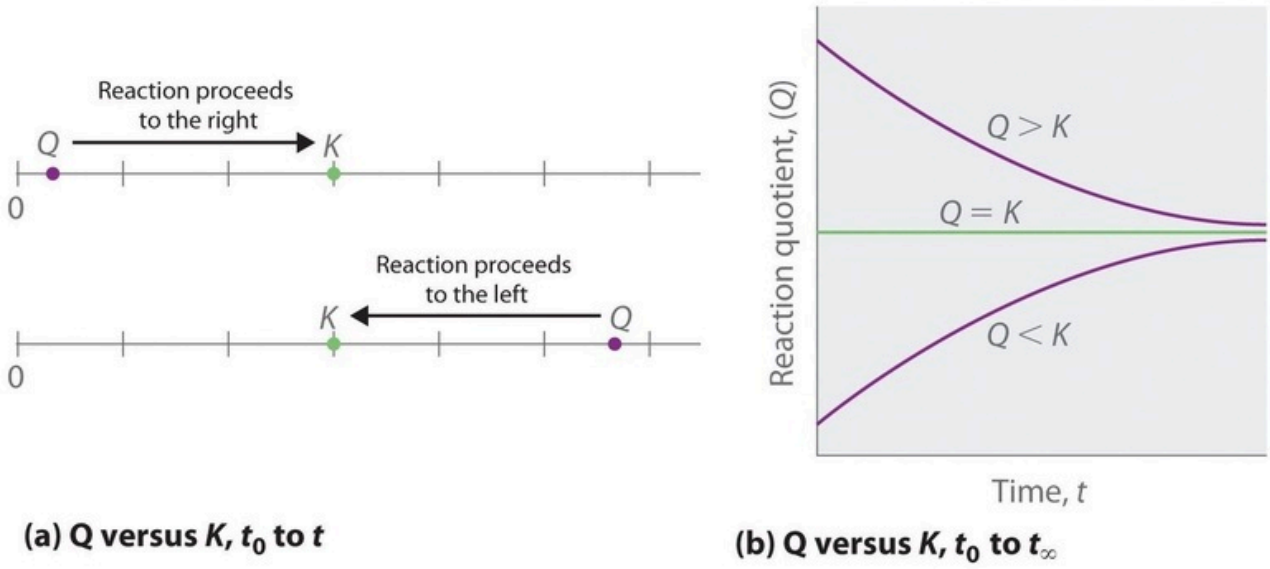


Figure $5.6.1$: Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K.(a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K. (b) The change in the composition of a system with time is illustrated for systems with initial values of $Q > K$, $Q < K$, and $Q = K$.

If $Q < K$, the reaction will proceed to the right as written. If $Q > K$, the reaction will proceed to the left as written. If $Q = K$, then the system is at equilibrium.

Example $5.6.1$: steam-reforming

At elevated temperatures, methane (CH_4) reacts with water to produce hydrogen and carbon monoxide in what is known as a steam-reforming reaction:

$$\mathrm{CH_4\,(g) + H_2O\,(g) \rightleftharpoons CO\,(g) + 3\,H_2\,(g)}$$

$K = 2.4 \times 10^{-4}$ at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If 1.2×10^{-2} mol of CH_4, 8.0×10^{-3} mol of H_2O, 1.6×10^{-2} mol of CO, and 6.0×10^{-3} mol of H_2 are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and H_2 or to the left to form CH_4 and H_2O?

Given: balanced chemical equation, K, amounts of reactants and products, and volume

Asked for: direction of reaction

Strategy:

A. Calculate the molar concentrations of the reactants and the products.
B. Use Equation 1.1.1 to determine Q. Compare Q and K to determine in which direction the reaction will proceed.

Solution:

A: We must first find the initial concentrations of the substances present. For example, we have $1.2 \times 10^{-2} mol$ of CH_4 in a 2.0 L container, so

$$[CH_4] = \frac{1.2 \times 10^{-2} mol}{2.0\ L} = 6.0 \times 10^{-3} M$$

We can calculate the other concentrations in a similar way:

- $[H_2O] = 4.0 \times 10^{-3} M$,
- $[CO] = 8.0 \times 10^{-3} M$, and
- $[H_2] = 3.0 \times 10^{-3} M$.

B: We now compute Q and compare it with K:

$$Q = \frac{[CO][H_2]^3}{[CH_4][H_2O]} = \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})} = 9.0 \times 10^{-6}$$

Because $K = 2.4 \times 10^{-4}$, we see that $Q < K$. Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming $\mathrm{H_2}$ and CO at the expense of H_2O and CH_4.

Exercise 5.6.1

In the water–gas shift reaction introduced in Example 5.6.1, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:

$$\mathrm{CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)}$$

$K = 0.64$ at 900 K. If 0.010 mol of both CO and $\mathrm{H_2O}$, 0.0080 mol of $\mathrm{CO_2}$, and 0.012 mol of $\mathrm{H_2}$ are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

Answer

$Q = 0.96$ (Q > K), so the reaction will proceed to the left, and CO and H_2O will form.

Predicting the Direction of a Reaction with a Graph

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which $Q = K$. Such a graph allows us to predict what will happen to a reaction when conditions change so that Q no longer equals K, such as when a reactant concentration or a product concentration is increased or decreased.

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:

Because $PbCO_3$ and PbO are solids, the equilibrium constant is simply $K = [CO_2]$. At a given temperature, therefore, any system that contains solid $PbCO_3$ and solid PbO will have exactly the same concentration of CO_2 at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure 5.6.2, which shows a plot of $[CO_2]$ versus the amount of $PbCO_3$ added. Initially, the added $PbCO_3$ decomposes completely to CO_2 because the amount of $PbCO_3$ is not sufficient to give a CO_2 concentration equal to K. Thus the left portion of the graph represents a system that is not at equilibrium because it contains only CO2(g) and PbO(s). In contrast, when just enough $PbCO_3$ has been added to give $[CO_2] = K$, the system has reached equilibrium, and adding more $PbCO_3$ has no effect on the CO_2 concentration: the graph is a horizontal line. Thus any CO_2 concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough $PbCO_3$ and PbO are present. For example, the point labeled A in Figure 5.6.2 lies above the horizontal line, so it corresponds to a $[CO_2]$ that is greater than the equilibrium concentration of CO_2 (Q > K). To reach equilibrium, the system must decrease $[CO_2]$, which it can do only by reacting CO_2 with solid PbO to form solid $PbCO_3$. Thus the reaction in Equation 1.1.5 will proceed to the left as written, until $[CO_2] = K$. Conversely, the point labeled B in Figure 5.6.2 lies below the horizontal line, so it corresponds to a $[CO_2]$ that is less than the equilibrium concentration of CO_2 (Q < K). To reach equilibrium, the system must increase $[CO_2]$, which it can do only by decomposing solid $PbCO_3$ to form CO_2 and solid PbO. The reaction in Equation 1.1.5 will therefore proceed to the right as written, until $[CO_2] = K$.

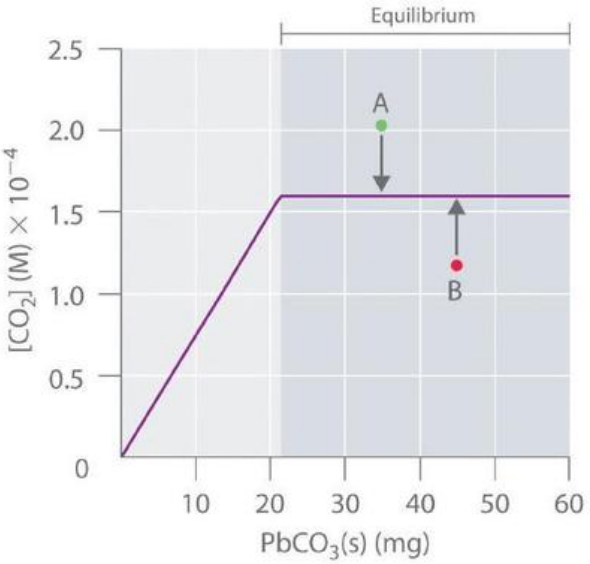


Figure 5.6.2: The Concentration of Gaseous CO_2 in a Closed System at Equilibrium as a Function of the Amount of Solid $PbCO_3$ Added. Initially the concentration of CO2(g) increases linearly with the amount of solid $PbCO_3$ added, as $PbCO_3$ decomposes to CO2(g) and solid PbO. Once the CO_2 concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $PbCO_3$ has no effect on $[CO_2]$, as long as the temperature remains constant.

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:

and the equilibrium constant K is $[H_2O]/[H_2]$. If $[H_2O]$ is doubled at equilibrium, then [H2] must also be doubled for the system to remain at equilibrium. A plot of $[H_2O]$ versus $[H_2]$ at equilibrium is a straight line with a slope of K (Figure 5.6.3). Again, only those pairs of concentrations of H_2O and H_2 that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a nonequilibrium state. In such cases, the reaction in Equation 2.1.969 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point A in Figure 5.6.3 lies below the line, indicating that the $[H_2O]/[H_2]$ ratio is less than the ratio of an equilibrium mixture (Q < K). Thus the reaction in Equation 2.1.969 will proceed to the right as written, consuming H_2 and producing H_2O, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point B in Figure 5.6.3 lies above the line, indicating that the $[H_2O]/[H_2]$ ratio is greater than the ratio of an equilibrium mixture (Q > K). Thus the reaction in Equation 2.1.969 will proceed to the left as written, consuming H_2O and producing H_2, which causes the concentration ratio to move down and to the right toward the equilibrium line.

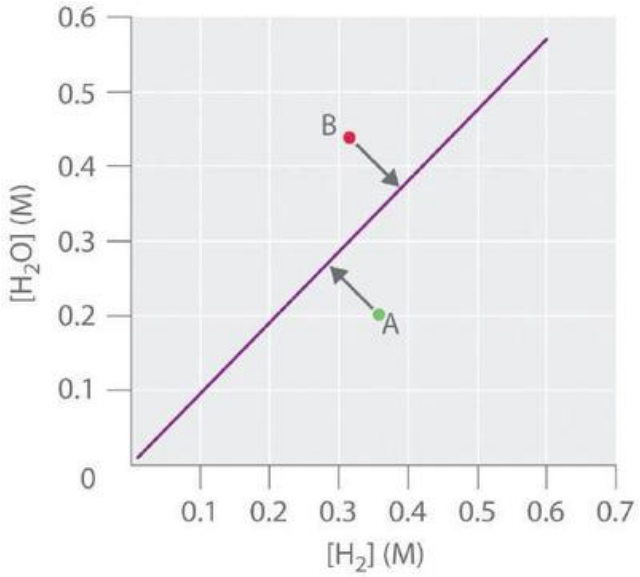


Figure 5.6.3: The Concentration of Water Vapor versus the Concentration of Hydrogen for the $CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)}$ System at Equilibrium. For any equilibrium concentration of $H_2O_{(g)}$, there is only one equilibrium concentration of H2(g). Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]$ at equilibrium requires a large $[H_2]$ and vice versa. In this case, the slope of the line is equal to K.

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:

[redacted]

For this system, K is equal to the product of the concentrations of the two products: $[NH_3][HI]$. If we double the concentration of NH3, the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure 5.6.4. As a result, for a given concentration of either HI or NH_3, only a single equilibrium composition that contains equal concentrations of both NH_3 and HI is possible, for which $[NH_3] = [HI] = K^{1/2}$. Any point that lies below and to the left of the equilibrium curve (such as point A in Figure 5.6.4) corresponds to $Q < K$, and the reaction in Equation 2.5.998 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point B in Figure 5.6.4) corresponds to $Q > K$, and the reaction in Equation 2.5.998 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

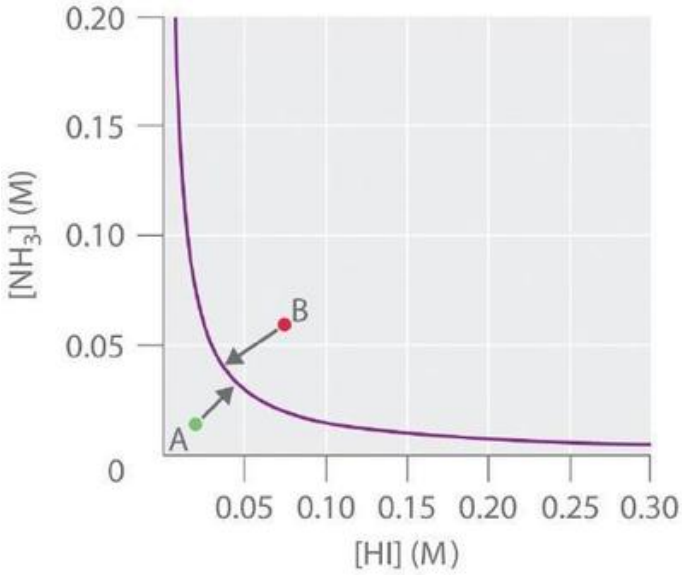


Figure 5.6.4: The Concentration of $NH_{3(g)}$ versus the Concentration of $HI_{(g)}$ for the $NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)}$ System at Equilibrium. Only one equilibrium concentration of $NH_{3(g)}$ is possible for any given equilibrium concentration of HI(g). In this case, the two are inversely proportional. Thus a large $[HI]$ at equilibrium requires a small $[NH_3]$ at equilibrium and vice versa.

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_p). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

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https://www.youtube.com/embed/pnU7ogsgUW8?vq=hd1080

Video $5.6.1$: See www.youtube.com/watch?v=pnU7ogsgUW8 to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, $\mathrm{O_2}$, and $\mathrm{NO_2}$ are at equilibrium:



The formation of additional amounts of $\mathrm{NO_2}$ decreases the total number of molecules in the system because each time two molecules of $\mathrm{NO_2}$ form, a total of three molecules of NO and $\mathrm{O_2}$ are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of $\mathrm{NO_2}$ into NO and $\mathrm{O_2}$, which tends to restore the pressure.

Now consider this reaction:



Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the Reaction Quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.



Because this reaction is exothermic, we can write it with heat as a product.

[redacted]

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of $\mathrm{H_2}$ and $\mathrm{I_2}$ and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of $\mathrm{H_2}$ and $\mathrm{I_2}$ decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between $\mathrm{NO_2}$ and $\mathrm{N_2O_4}$ in this reaction

[redacted]

The positive ΔH value tells us that the reaction is endothermic and could be written

[redacted]

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown $\mathrm{NO_2}$ molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless $\mathrm{N_2O_4}$ increases, and the concentration of brown $\mathrm{NO_2}$ decreases, causing the brown color to fade.

Temperature is Neither a Reactant nor Product

It is not uncommon that textbooks and instructors to consider heat as a independent "species" in a reaction. While this is rigorously incorrect because one cannot "add or remove heat" to a reaction as with species, it serves as a convenient mechanism to predict the shift of reactions with changing temperature. For example, if heat is a "reactant" ($\Delta H > 0$), then the reaction favors the formation of products at elevated temperature. Similarly, if heat is a "product" ($\Delta H < 0$), then the reaction favors the formation of reactants. A more accurate, and hence preferred, description is discussed below.

Example 5.6.2: Steam Reforming of Methane

The commercial production of hydrogen is carried out by treating natural gas with steam at high temperatures and in the presence of a catalyst (“steam reforming of methane”):

$$\mathrm{CH_4 + H_2O \rightleftharpoons CH_3OH + H_2}$$

Given the following boiling points: CH_4 (methane) = –161°C, H_2O = 100°C, CH_3OH = 65°, H_2 = –253°C, predict the effects of an increase in the total pressure on this equilibrium at 50°, 75° and 120°C.

Solution

To identify the influence of changing pressure on the three reaction conditions, we need to identify the correct reaction including the phase of each reactant and product. Calculate the change in the moles of gas for each process:

Temperature		
Equation	Δn_g	shift

50° $[CH_4(g) + H_2O(l) \longrightarrow CH_3OH(l) + H_2(g)$ 0 none 75° $CH_4(g) + H_2O(l) \longrightarrow CH_3OH(g) + H_2(g)$ +1 to left 120° $CH_4(g) + H_2O(g) \longrightarrow CH_3OH(g) + H_2(g)$ 0 none

Exercise 5.6.2

What will happen to the equilibrium when the volume of the system is decreased?

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

Answer

Decreasing the volume leads to an increase in pressure which will cause the equilibrium to shift towards the side with fewer moles. In this reaciton, there are three moles on the reactant side and two moles on the product side, so the new equilibrium will shift towards the products (to the right).

Summary

The Reaction Quotient (Q) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction. Reaction Quotient:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The Reaction Quotient (Q or Q_p) has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium, $Q = K$. Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium.

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Footnotes

1. 1 Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle
: when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium
: concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress
: change to a reaction's conditions that may cause a shift in the equilibrium

Contributors and Attributions

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5.7: The Direction of Change in Chemical Reactions - Thermodynamic Explanation

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously:

- $\Delta S_{univ} > 0$ (2nd law of thermodynamics),
- $\Delta G_{sys} < 0$ (Gibbs Energy version), and
- the relative magnitude of the reaction quotient Q versus the equilibrium constant K.

Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table $5.7.1$ summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table $5.7.1$: Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
$Q < K$	$Q = K$	$Q > K$
***Spontaneous in the reverse direction.**		

Because all three criteria assess the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the standard free energy of reaction (ΔG°) and the equilibrium constant (K).

Free Energy and the Equilibrium Constant

Because ΔH° and ΔS° determine the magnitude of ΔG° and because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG° and vice versa. "Free Energy", ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. The general relationship can be shown as follow (derivation not shown):

[redacted]

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation $5.7.1178$ simplifies to

[redacted]

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the V in Equation $5.7.1179$ by nRT/P (where n is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f, respectively):

[redacted]

If the initial state is the standard state with P_i = 1 atm, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G^\circ = nRT \ln P \tag{5.7.1603}$$

This can be rearranged as follows:

[redacted]

As you will soon discover, Equation 5.7.1183 allows us to relate ΔG^o and K_p. Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

[redacted]

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

[redacted]

Substituting Equation 5.7.1183 for each term into Equation 5.7.1186,

$$\Delta G = [(cG^o_C + cRT \ln P_C) + (dG^o_D + dRT \ln P_D)] - [(aG^o_A + aRT \ln P_A) + (bG^o_B + bRT \ln P_B)] \tag{5.7.1605}$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

[redacted]

where ΔG° indicates that all reactants and products are in their standard states. For gases at equilibrium ($Q = K_p$,), and as you've learned in this chapter, $\Delta G = 0$ for a system at equilibrium. Therefore, we can describe the relationship between ΔG^o and K_p for gases as follows:

[redacted]

If the products and reactants are in their standard states and $\Delta G^\circ < 0$, then $K_p > 1$, and products are favored over reactants. Conversely, if $\Delta G^\circ > 0$, then $K_p < 1$, and reactants are favored over products. If $\Delta G^\circ = 0$, then $K_p = 1$, and neither reactants nor products are favored: the system is at equilibrium.

> For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of Q), equilibrium is established when the system's free energy is minimized (Figure 5.7.3). If a system is present with reactants and products present in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

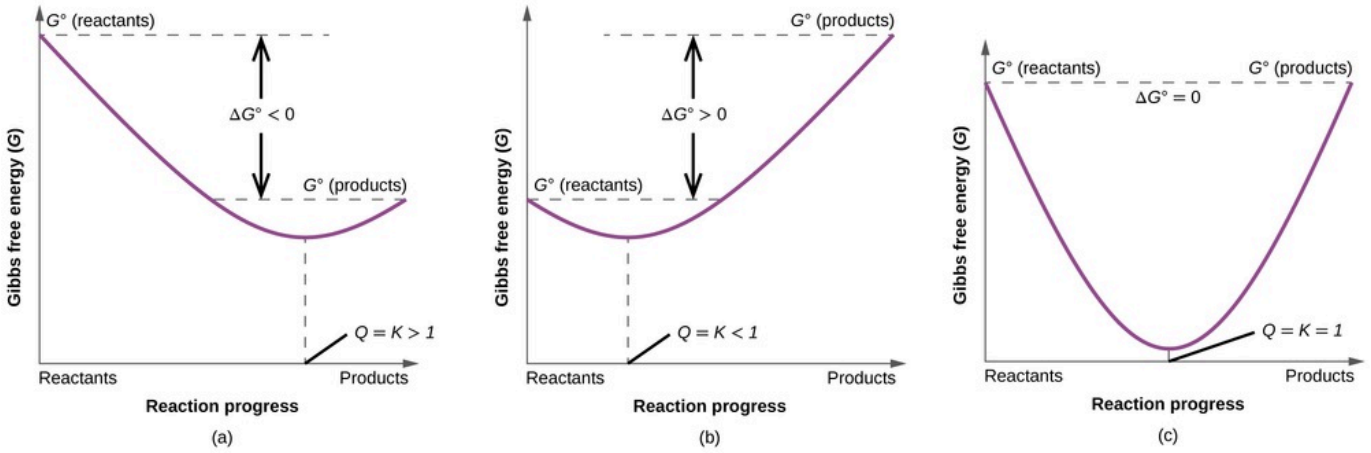


Figure 5.7.1: These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium. (CC BY 4.0; OpenStax).

Example 5.7.2

ΔG^o is –32.7 kJ/mol of N_2 for the reaction

$$\mathrm{N_2\,(g) + 3\,H_2\,(g)} \rightleftharpoons \mathrm{2\,NH_3\,(g)}$$

This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions:

- P_{N_2} = 2.00 atm,
- P_{H_2} = 7.00 atm,
- P_{NH_3} = 0.021 atm,
- and T = 100°C.

Does the reaction favor products or reactants?

Given: balanced chemical equation, partial pressure of each species, temperature, and ΔG°

Asked for: whether products or reactants are favored

Strategy:

A. Using the values given and Equation 5.7.1189, calculate Q.
B. Substitute the values of ΔG° and Q into Equation 5.7.1189 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG° and ΔG under nonstandard conditions is given in Equation 5.7.1189. Substituting the partial pressures given, we can calculate Q:

$$Q = \frac{P^2_{NH_3}}{P_{N_2}P^3_{H_2}} = \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7}$$

B Substituting the values of ΔG° and Q into Equation 5.7.1189,

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT\ln Q \\ &= -32.7\text{ kJ} + \left[(8.314\text{ J/K})(373\text{ K})\left(\frac{1\text{ kJ}}{1000\text{ J}}\right)\ln(6.4\times10^{-7})\right] \\ &= -32.7\text{ kJ} + (-44\text{ kJ}) \\ &= -77\text{ kJ/mol of } N_2\end{aligned}$$

Because ΔG < 0 and Q < 1.0, the reaction is spontaneous to the right as written, so products are favored over reactants.

Exercise 5.7.2

Calculate ΔG for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: T = 50°C, P_{NO} = 0.0100 atm, P_{O_2} = 0.200 atm, and $P_{NO_2} = 1.00\times10^{-4}$ atm. The value of ΔG° for this reaction is –72.5 kJ/mol of O_2. Are products or reactants favored?

Answer

–92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written, so products are favored.

Example 5.7.3

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C. ΔG^o for this reaction is –32.7 kJ/mol of N_2.

Given: balanced chemical equation from Example 5.7.2, ΔG°, and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG° and T (in kelvin) into Equation 5.7.1191 to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution

In Example 10, we used tabulated values of ΔG°_f to calculate ΔG° for this reaction (–32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 5.7.1191,

$$\Delta G^\circ = -RT\ln K_p$$
$$\frac{-\Delta G^\circ}{RT} = \ln K_p$$

Inserting the value of ΔG° and the temperature (25°C = 298 K) into this equation,

$$\ln K_p = -\frac{(-32.7\text{ kJ})(1000\text{ J/kJ})}{(8.314\text{ J/K})(298\text{ K})} = 13.2$$
$$K_p = 5.4\times10^5$$

Thus the equilibrium constant for the formation of ammonia at room temperature is favorable. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

Exercise 5.7.3

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. ΔG° for this reaction is –70.5 kJ/mol of O_2.

Answer

2.2×10^{12}

Although K_p is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant K is defined in terms of the concentrations of the reactants and the products. We described the relationship between the numerical magnitude of \(K_p\) and K previously and showed that they are related:

[redacted]

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 5.7.1191 can be written in a more general form:

[redacted]

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 5.7.1193 for the difference between K_p and K. Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of **activities** or **fugacities** in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

Combining Equations 5.7.1193 with $\Delta G^o = \Delta H^o - T\Delta S^o$ provides insight into how the components of ΔG° influence the magnitude of the equilibrium constant:

[redacted]

Notice that K becomes larger as ΔS° becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as ΔH° decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

> The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder and seek the lowest energy state possible.

Temperature Dependence of the Equilibrium Constant

The fact that ΔG° and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 5.7.1194, which can be rearranged as follows:

[redacted]

Assuming ΔH° and ΔS° are temperature independent, for an exothermic reaction (ΔH° < 0), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction (ΔH° > 0), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 5.7.1195 agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 5.7.1195 also shows that the magnitude of ΔH° dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS° affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH° for a reaction, we can estimate the value of K at any other

temperature, even in the absence of information on ΔS°. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying Equation 5.7.1195 gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \tag{5.7.1607}$$

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \tag{5.7.1608}$$

Subtracting $\ln K_1$ from $\ln K_2$,

[redacted]

Thus calculating ΔH° from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH° and ΔS° are independent of temperature. Equation 5.7.1198 is often referred to as the **van 't Hoff equation** after Dutch chemist Jacobus Henricus van 't Hoff in 1884 in his book Études de Dynamique chimique (Studies in dynamic chemistry).

Example 5.7.4

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C was calculated to be $K_p = 5.4 \times 10^5$ in Example 5.7.2. What is K_p at 500°C? (Use the data from Example 5.7.1)

Given: balanced chemical equation, ΔH°, initial and final T, and K_p at 25°C

Asked for: K_p at 500°C

Strategy:

Convert the initial and final temperatures to kelvin. Then substitute appropriate values into Equation 5.7.1198 to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of ΔH° for the reaction obtained using Hess's law is −91.8 kJ/mol of N_2. If we set T_1 = 25°C = 298 K and T_2 = 500°C = 773 K, then from Equation 5.7.1198 we obtain the following:

$$\begin{aligned}
\ln \frac{K_2}{K_1} &= \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \\
&= \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{8.314\ \text{J/K}}\left(\frac{1}{298\ \text{K}} - \frac{1}{773\ \text{K}}\right) = -22.8 \\
\frac{K_2}{K_1} &= 1.3 \times 10^{-10} \\
K_2 &= (5.4 \times 10^5)(1.3 \times 10^{-10}) = 7.0 \times 10^{-5}
\end{aligned}$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

Exercise 5.7.4

The equilibrium constant for the reaction of NO with O_2 to give NO_2 at 25°C is $K_p = 2.2 \times 1012$. Use the ΔH_f^o values in the exercise in Example 5.7.4 to calculate K_p for this reaction at 1000°C.

Answer

5.6×10^{-4}

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial pressures of the reactants and products, which gives us a relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If ΔG° < 0, then K or K_p > 1, and products are favored over reactants. If ΔG° > 0, then K or K_p < 1, and reactants are favored over products. If ΔG° = 0, then K or K_p = 1, and the system is at equilibrium. We can use the measured equilibrium constant K at one temperature and ΔH° to estimate the equilibrium constant for a reaction at any other temperature.

Contributors and Attributions

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5.8: Distribution between Immiscible Phases - Extraction and Separation Processes

A partitioning of a compound exist between a mixture of two immiscible phases at equilibrium, which is a measure of the difference in solubility of the compound in these two phases. If one of the solvents is a gas and the other a liquid, the "gas/liquid partition coefficient" is the same as the dimensionless form of the Henry's law constant. A solute can partition when one or both solvents is a solid (e.g., solid solution).

Liquid-Liquid Extractions

We call the process of moving a species from one phase to another phase an **extraction**. Simple extractions are particularly useful for separations where only one component has a favorable partition coefficient. Several important separation techniques are based on a simple extraction, including liquid–liquid, liquid–solid, solid–liquid, and gas–solid extractions. The most important group of separation techniques uses a selective partitioning of the solute between two immiscible phases. If we bring a phase containing a solute, S, into contact with a second phase, the solute partitions itself between the two phases, as shown by the following equilibrium reaction.



The equilibrium constant for this equilbrium is

$$K_{\mathrm{D}} = \frac{[\mathrm{S}_{\text{phase 2}}]}{[\mathrm{S}_{\text{phase 1}}]} \tag{5.8.1609}$$

is called the distribution constant or **partition coefficient**. If K_D is sufficiently large, then the solute moves from phase 1 to phase 2. The solute remains in phase 1 if the partition coefficient is sufficiently small. When we bring a phase containing two solutes into contact with a second phase, if K_{D} is favorable for only one of the solutes a separation of the solutes is possible. The physical states of the phases are identified when describing the separation process, with the phase containing the sample listed first. For example, if the sample is in a liquid phase and the second phase is a solid, then the separation involves liquid–solid partitioning.

It often happens that two immiscible liquid phases are in contact, one of which contains a solute. How will the solute tend to distribute itself between the two phases? One's first thought might be that some of the solute will migrate from one phase into the other until it is distributed equally between the two phases, since this would correspond to the maximum dispersion (randomness) of the solute. This, however, does not take into the account the differing solubilities the solute might have in the two liquids; if such a difference does exist, the solute will preferentially migrate into the phase in which it is more soluble (Figure $5.8.1$).

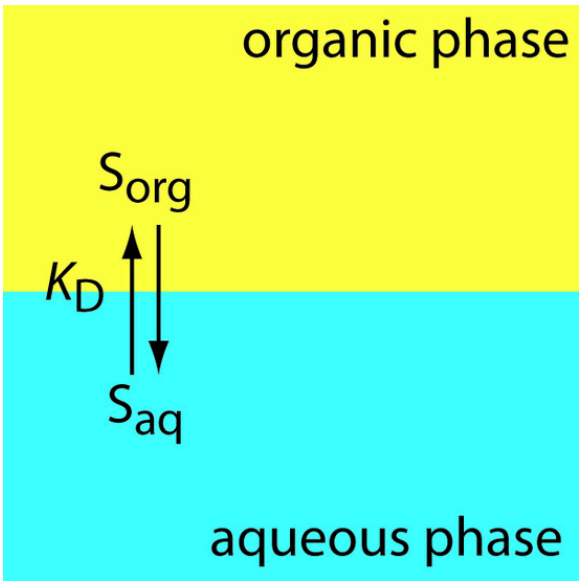


Figure 5.8.1: Scheme for a simple liquid–liquid extraction in which the solute's partitioning depends only on the K_D equilibrium.

Biomagnification

The transport of substances between different phases is of immense importance in such diverse fields as pharmacology and environmental science. For example, if a drug is to pass from the aqueous phase with the stomach into the bloodstream, it must pass through the lipid (oil-like) phase of the epithelial cells that line the digestive tract. Similarly, a pollutant such as a pesticide residue that is more soluble in oil than in water will be preferentially taken up and retained by marine organism, especially fish, whose bodies contain more oil-like substances; this is basically the mechanism whereby such residues as DDT can undergo *biomagnification* as they become more concentrated at higher levels within the food chain. For this reason, environmental regulations now require that oil-water distribution ratios be established for any new chemical likely to find its way into natural waters. The standard "oil" phase that is almost universally used is octanol, $C_8H_{17}OH$.

In preparative chemistry it is frequently necessary to recover a desired product present in a reaction mixture by extracting it into another liquid in which it is more soluble than the unwanted substances. On the laboratory scale this operation is carried out in a **separatory funnel** as shown below. The two immiscible liquids are poured into the funnel through the opening at the top. The funnel is then shaken to bring the two phases into intimate contact, and then set aside to allow the two liquids to separate into layers, which are then separated by allowing the more dense liquid to exit through the stopcock at the bottom.



Figure 5.8.2: A separatory funnel with two solvents.

If the distribution ratio is too low to achieve efficient separation in a single step, it can be repeated; there are automated devices that can carry out hundreds of successive extractions, each yielding a product of higher purity. In these applications our goal is to exploit the Le Chatelier principle by repeatedly upsetting the phase distribution equilibrium that would result if two phases were to remain in permanent contact.

YouTube Video

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https://www.youtube.com/embed/vcwfhDhLiQU?vq=hd1080

Video 5.8.1: How to perform a liquid-liquid extraction using a separating funnel.

Example 5.8.1

The distribution ratio for iodine between water and carbon disulfide is 650. Calculate the concentration of I_2 remaining in the aqueous phase after 50.0 mL of 0.10M I_2 in water is shaken with 10.0 mL of CS_2.

Solution

The equilibrium constant is

$$K_d = \frac{C_{CS_2}}{C_{H_2O}} = 650$$

Let m_1 and m_2 represent the numbers of millimoles of solute in the water and CS_2 layers, respectively. K_d can then be written as (m_2/10 mL) ÷ (m_1/50 mL) = 650. The number of moles of solute is (50 mL) × (0.10 mmol mL^{-1}) = 5.00 mmol, and mass conservation requires that $m_1 + m_2$ = 5.00 mmol, so m_2 = (5.00 – m_1) mmol and we now have only the single unknown m_1. The equilibrium constant then becomes

$$\frac{(5.00–m_1)\,mmol/10\,mL}{m_1\,mmol/50\,mL} = 650$$

Simplifying and solving for m_1 yields

$$\frac{(0.50–0.1)m_1}{0.02\,m_1} = 650$$

with m_1 = 0.0382 mmol.

The concentration of solute in the water layer is (0.0382 mmol) / (50 mL) = **0.000763 M**, showing that almost all of the iodine has moved into the CS_2 layer.

Chromatographic Separations

In an extraction, the sample is one phase and we extract the analyte or the interferent into a second phase. We also can separate the analyte and interferents by continuously passing one sample-free phase, called the mobile phase, over a second sample-free phase that remains fixed or stationary. The sample is injected into the mobile phase and the sample's components partition themselves between the mobile phase and the stationary phase. Those components with larger partition coefficients are more likely to move into the stationary phase, taking a longer time to pass through the system. This is the basis of all chromatographic separations. Chromatography provides both a separation of analytes and interferents, and a means for performing a qualitative or quantitative analysis for the analyte.

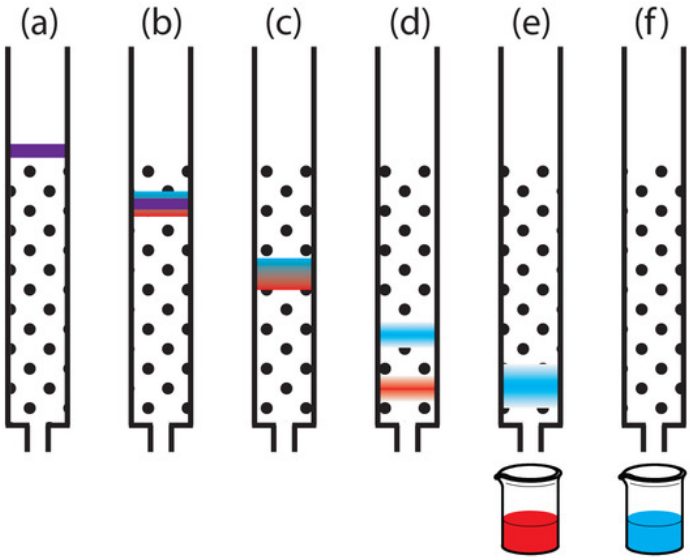


Figure 5.8.3: Progress of a column chromatographic separation of a two-component mixture. In (a) the sample is layered on top of the stationary phase. As mobile phase passes through the column, the sample separates into two solute bands (b–d). In (e) and (f), we collect each solute as it elutes from the column.

Of the two methods for bringing the stationary phase and the mobile phases into contact, the most important is column chromatography. In this section we develop a general theory that we may apply to any form of column chromatography. Figure 5.8.3 provides a simple view of a liquid–solid column chromatography experiment. The sample is introduced at the top of the column as a narrow band. Ideally, the solute's initial concentration profile is rectangular (Figure 5.8.1a). As the sample moves down the column the solutes begin to separate (Figures 5.8.1b, c), and the individual solute bands begin to broaden and develop a Gaussian profile. If the strength of each solute's interaction with the stationary phase is sufficiently different, then the solutes separate into individual bands (Figure 5.8.1d).

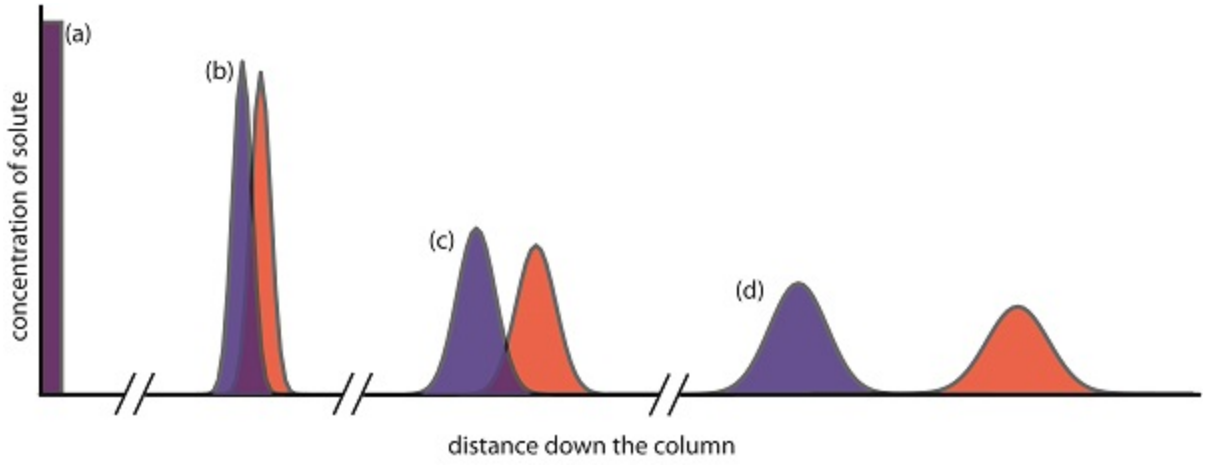


Figure 5.8.4: An alternative view of the separation in Figure 5.8.3 showing the concentration of each solute as a function of distance down the column.

We can follow the progress of the separation either by collecting fractions as they elute from the column (Figure 5.8.4), or by placing a suitable detector at the end of the column. A plot of the detector's response as a function of elution time, or as a function of the volume of mobile phase, is known as a **chromatogram** (Figure 5.8.5), and consists of a peak for each solute.

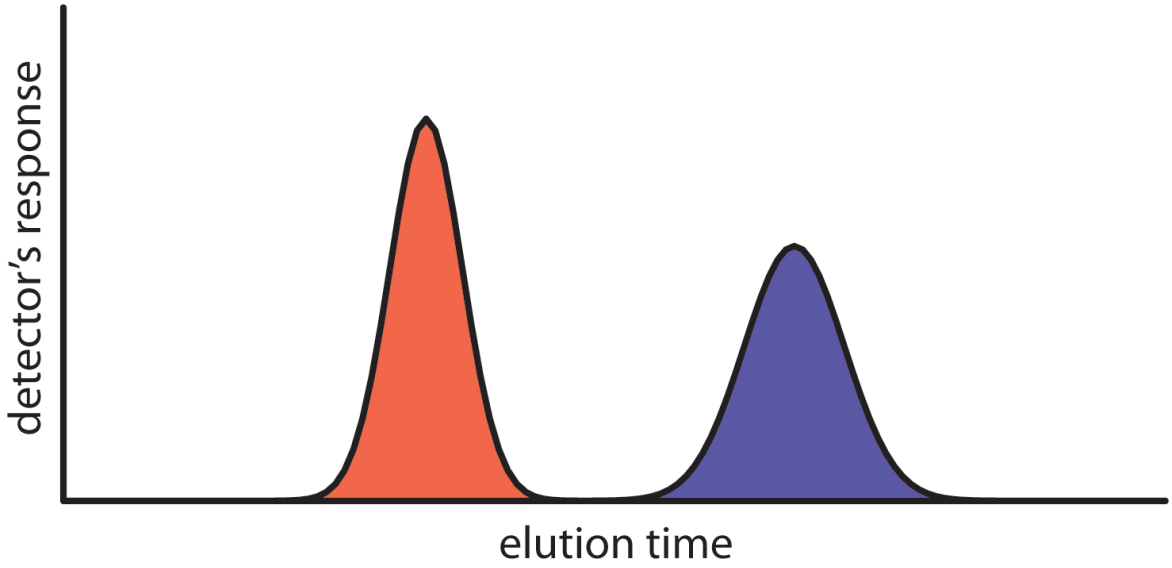


Figure 5.8.5: Chromatogram for the separation shown in Figure 5.8.3 showing the detector's response as a function of the elution time.

Contributors and Attributions

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5.E: Chemical Equilibrium (Exercises)

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

Q1

Write an expression for the equilibrium constant K_c for each reaction below.

a. $2\,\mathrm{NO}\,(\mathrm{g}) + \mathrm{O_2}\,(\mathrm{g}) \rightleftharpoons 2\,\mathrm{NO_2}\,(\mathrm{g})$
b. $\mathrm{N_2H_4}\,(\mathrm{g}) + 3\,\mathrm{O_2}\,(\mathrm{g}) \rightleftharpoons 2\,\mathrm{NO_2}\,(\mathrm{g}) + \mathrm{H_2O}\,(\mathrm{g})$
c. $\mathrm{O_3}\,(\mathrm{g}) + \mathrm{H_2O}\,(\mathrm{l}) \rightleftharpoons \mathrm{H_2}\,(\mathrm{g}) + 2\,\mathrm{O_2}\,(\mathrm{g})$

Solution

For a general reaction $a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons c\,\mathrm{C} + d\,\mathrm{D}$ then Law of Mass Action argues we can construct an equilibrium constant thusly

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

This is the general equations to substitute the reactants and product concentrations (with coefficients as exponents).

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

a. $K_c = \dfrac{[NO2]^2}{[NO]^2[O2]}$
b. $K_c = \dfrac{[H2O][NO2]^2}{[N2H4][O2]^3}$
c. $K_c = \dfrac{[O2]^2[H2]}{[O3]}$

Note that for part c, $\mathrm{H_2O}\,(\mathrm{l})$ is not included because pure solids and liquids are not included in the equilibrium constant.

Q3

Gaseous chlorine reacts with water vapor to form hydrogen chloride and oxygen gas. Write down the equilibrium expression (K_p) for the reaction.

Solution

First, a balanced reaction is constructed to ensure the equilibrium expression will be correctly states.

$$2\,\mathrm{Cl_2} + 2\,\mathrm{H_2O} \rightleftharpoons 4\,\mathrm{HCl} + \mathrm{O_2}$$

Equilibrium expression K_p is as follows:

$$K_p = \frac{p_{\mathrm{HCl}}^4 p_{\mathrm{O_2}}}{p_{\mathrm{Cl_2}}^2 p_{\mathrm{H_2O}}^2}$$

Q11

For each thermodynamics equilibrium expressions outlined below, determine one possible chemical reaction related to each.

a. $$K = \frac{a\{\mathrm{CO}\}^2}{a\{\mathrm{CO_2}\}}$$

b. $$K = \frac{a\{\mathrm{H_2O}\}^2}{a\{\mathrm{H_2}\}^2 a\{\mathrm{O_2}\}}$$

c. $$K = \frac{a\{\mathrm{Cl_2O}\}^2}{a\{\mathrm{Cl_2}\}^2 a\{\mathrm{O_2}\}}$$

d. $$K = \frac{a\{\mathrm{COCl_2}\}}{a\{\mathrm{CO}\} \cdot a\{\mathrm{Cl_2}\}}$$

Solution

a. $\mathrm{CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)}$

b. $\mathrm{2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g)}$

c. $\mathrm{2\,Cl_2(g) + O_2(g) \rightleftharpoons 2\,Cl_2O(g)}$

d. $\mathrm{CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)}$

Q15A

Based on the following data, calculate the equilibrium constant and the value of ΔG at 273 K.

a. $\mathrm{CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)}$ with

- $[\mathrm{CO_2}]_{\mathrm{eq}} = 0.0954\ \mathrm{M}$
- $[\mathrm{H_2}]_{\mathrm{eq}} = 0.0454\ \mathrm{M}$
- $[\mathrm{CO}]_{\mathrm{eq}} = 0.0046\ \mathrm{M}$
- $[\mathrm{H_2O}]_{\mathrm{eq}} = 0.0046\ \mathrm{M}$

b. $\mathrm{2\,NO(g) + 2\,H_2(g) \rightleftharpoons N_2(g) + 2\,H_2O(g)}$ with

- $[\mathrm{NO}]_{\mathrm{eq}} = 0.45\ \mathrm{M}$
- $[\mathrm{H_2}]_{\mathrm{eq}} = 0.63\ \mathrm{M}$
- $[\mathrm{N_2}]_{\mathrm{eq}} = 0.95\ \mathrm{M}$
- $[\mathrm{H_2O}]_{\mathrm{eq}} = 1.3\ \mathrm{M}$

Solution

a)

$$K = \frac{[\mathrm{CO}][\mathrm{H_2O}]}{[\mathrm{CO_2}][\mathrm{H_2}]} = \frac{(0.0046)(0.0046)}{(0.0954)(0.0454)} = 4.9 \times 10^{-3}$$

$$\Delta G = RT\ln(K) = (8.3145\,\mathrm{J/(K\ mol)})(273\,\mathrm{K})\ln(4.9 \times 10^{-3}) = -12072.288\,\mathrm{J/mol}$$

b)

$$K = \frac{[\mathrm{N_2}][\mathrm{H_2O}]^2}{[\mathrm{NO}]^2[\mathrm{H_2}]^2} = \frac{[0.95][1.3]^2}{[0.45]^2[0.63]^2} = 19.98$$

$$\Delta G = RT\ln(K) = (8.3145\,\mathrm{J/K\ mol})(273\,\mathrm{K})\ln(19.98) = 6797.62\,\mathrm{J/mol}$$

Q15B

Calculate the appropriate K value for the following reactions using the information provided. Assume that they are preformed under standard conditions (and 298.15 K).

a. $$2\,\mathrm{NO_2\,(g)} \rightleftharpoons 2\,\mathrm{NO\,(g)} + \mathrm{O_2\,(g)}$$

b. $$\mathrm{NH_4{}^+\,(aq)} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \mathrm{NH_3\,(aq)}$$

c. Jim's brother, Txeltoqlztop, goes to the bathroom only to find out that his sibling did not refill the toilet paper roll! To get revenge, Txeltoqlztop decides to fill his brother's room with carbon monoxide, via the following reaction:

$$2\,\mathrm{CH_4\,(g)} + 3\,\mathrm{O_2\,(g)} \rightleftharpoons 2\,\mathrm{CO\,(g)} + 4\,\mathrm{H_2O\,(g)}$$

Calculate the K value for this equation under standard conditions, interpret what it means in regards to the direction this equation will go, and compare it to the other two.

Solution

The core of this problem is to find the K value and understanding what information it can describe about the reaction. Since the problem provides many, many ΔG_f, it is likely that to calculate the K value, a relationship needs to be drawn from ΔG to K. This relationship is as follows:

$$\Delta G^\circ_{\mathrm{rxn}} = -RT\ln\left(K_p\right)$$

Relevant Information obtained from the thermodynamic tables

$\Delta G^\circ_f\ \mathrm{NO_2\,(g)} = 51.30\dfrac{\mathrm{kJ}}{\mathrm{mol}}$ $\Delta G^\circ_f\ \mathrm{H_3O^+\,(aq)} = -103.45\dfrac{\mathrm{kJ}}{\mathrm{mol}}$

$\Delta G^\circ_f\ \mathrm{NO\,(g)} = 86.57\dfrac{\mathrm{kJ}}{\mathrm{mol}}$ $\Delta G^\circ_f\ \mathrm{NH_3\,(aq)} = -26.5\dfrac{\mathrm{kJ}}{\mathrm{mol}}$

$\Delta G^\circ_f\ \mathrm{O_2\,(g)} = 0\dfrac{\mathrm{kJ}}{\mathrm{mol}}$ $\Delta G^\circ_f\ \mathrm{CH_4\,(g)} = -50.84\dfrac{\mathrm{kJ}}{\mathrm{mol}}$

$\Delta G^\circ_f\ \mathrm{NH_4{}^+\,(aq)} = -79.37\dfrac{\mathrm{kJ}}{\mathrm{mol}}$ $\Delta G^\circ_f\ \mathrm{CO\,(g)} = -137.28\dfrac{\mathrm{kJ}}{\mathrm{mol}}$

$\Delta G^\circ_f\ \mathrm{H_2O\,(l)} = -237.14\dfrac{\mathrm{kJ}}{\mathrm{mol}}$ $\Delta G^\circ_f\ \mathrm{H_2O\,(g)} = -228.61\dfrac{\mathrm{kJ}}{\mathrm{mol}}$

Note that the relationship here is between ΔG and K_p, which is:

$$K_p \approx \frac{P_{\mathrm{products}}}{P_{\mathrm{reactants}}}$$

Where P is partial pressure of the products or reactants. The reason this is an approximation is because the equilibrium actually measures the *activities* of the species, but by using just the partial pressures a good estimate is procured. Since the equation relating K_p and ΔG only has these two variables as unknown, once ΔG is found, algebra can find K_p . The process for utilizing Hess's Law to find state variables is outlined extensively. The values below were found using the exact same process, now for ΔG (Just in case, the Hess law formula is provided).

$$\Delta G^\circ = \sum n_{\mathrm{products}} \times \Delta G^\circ_{f_{\mathrm{products}}} - \sum n_{\mathrm{reactants}} \times \Delta G^\circ_{f_{\mathrm{reactants}}}$$

$$\Delta G^\circ(2\,\mathrm{NO_2(g)} \rightleftharpoons 2\,\mathrm{NO\,(g)} + \mathrm{O_2\,(g)}) = 70.42\ \frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\Delta G^\circ(\mathrm{NH_4{}^+\,(aq)} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \mathrm{NH_3\,(aq)}) = -437.93\frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\Delta G^\circ(2\,\mathrm{CH_4\,(g)} + 3\,\mathrm{O_2\,(g)} \rightleftharpoons 2\,\mathrm{CO\,(g)} + 4\,\mathrm{H_2O\,(l)}) = -1121.44\frac{\mathrm{kJ}}{\mathrm{mol}}$$

To find K, plug in the ΔG into the equation above. (Note that the solution does NOT show the conversion of the gas constant from J to kJ!!)

$$\Delta G^\circ_{\mathrm{rxn}} = -\left(8.314\,\frac{\mathrm{J}}{\mathrm{mol\,K}}\right)(298.15\,\mathrm{K}) \times \ln\left(K_p\right)$$

$$70.54\frac{\mathrm{kJ}}{\mathrm{mol}} = -\left(8.314\frac{\mathrm{J}}{\mathrm{mol\,K}}\right)(298.15\,\mathrm{K}) \times \ln\left(K_p\right)$$

$$-\frac{70.54\,\frac{\text{kJ}}{\text{mol}}}{\left(8.314\frac{\text{J}}{\text{molK}}\right)(298.15\,\text{K})} = \ln(K_p)$$

$$e^{-\frac{70.54\,\frac{\text{kJ}}{\text{mol}}}{\left(8.314\frac{\text{J}}{\text{mol K}}\right)(298.15\,\text{K})}} = K_p$$

$$K_p \approx e^{-28.457} \approx 4.3776 \times 10^{-13}$$

Thus, the K_p value for $2\,\text{NO}_2\,(\text{g}) \rightleftharpoons 2\,\text{NO}\,(\text{g}) + \text{O}_2\,(\text{g})$ is a very small number!. Since the equilibrium value depicts the ratio of products to reactants at the equilibrium point, this very tiny K_p value means that the reaction will heavily favor the reactants. The third reaction where Txeltoqlztop wants to poison his brother with CO also follows the same process, and the answer is such:

$$K_p \approx e^{452}$$

e^{452} is a *really* big number! That means, while the previous reaction will stay mostly on the reactant sides, this reaction heavily favors the products side, meaning that pretty much all of the methane and oxygen that Txeltoqlztop uses will be transformed into carbon monoxide, which is all the better for him!

The same method can be applied to the aqueous reaction, but the K value calculated is K_c rather than K_p.

$$K_c \approx e^{-176.65} \approx 1.898 \times 10^{-77}*$$

*These equilibrium constants are based solely off the calculated Gibbs energy, some of the reactions, therefore, may have actual K values much different from the ones calculated.

Abstract: use of $\Delta G^\circ_{\text{rxn}} = -RT \times \ln(K_p)$

Q15C

Use the thermodynamic data in Tables T1 and T2 to calculate the equilibrium constants for the following equations at 25°C.

a. $\text{H}_2\,(\text{g}) + 2\,\text{F}\,(\text{g}) \rightleftharpoons 2\,\text{HF}\,(\text{g})$
b. $\text{FeCl}_3\,(\text{s}) \rightleftharpoons \text{FeCl}_2\,(\text{s}) + \text{Cl}_2\,(\text{g})$
c. $\text{CaSO}_4\,(\text{s}) \rightleftharpoons \text{Ca}^{2+}\,(\text{aq}) + \text{SO}_4{}^{2-}\,(\text{aq})$

Solution

For each of the chemical reactions, the main equation needed is

$$\Delta G_{\text{rxn}} = -R \times T \times \ln K$$

Where R is 8.134 J K^{-1} mol^{-1} and T is equal to 298K. In order to determine the value of G_{rxn}, the following the reaction is needed

$$\Delta G_{\text{rxn}} = \sum nG^\circ_f(\text{products}) - \sum nG^\circ_f(\text{reactants})$$

a. By looking in the tables, the ΔG of formation can be found and they are listed for each compound below

$H_2(g)$ = 203.3 J mol^{-1}, $F_2(g)$ = 62.3 J mol^{-1}, HF(g)=-275.4 J mol^{-1}

Next, these values are plugged into the second equation to the the change in Gibbs energy for the reaction

$$\Delta G_{\text{rxn}} = -275.4\ \text{J mol}^{-1} - (203.3\ \text{J mol}^{-1} + 62.3\ \text{J mol}^{-1}) = -514\ \text{J mol}^{-1}$$

Using the the value for the Gibbs Energy, the value of K can be determined using the first equation

$$-541\ \text{J mol}^{-1} = -8.314\ \text{J K}^{-1}\text{mol}^{-1} \times 298\ \text{K} \times \ln K$$

$$\frac{-541\ \text{J mol}^{-1}}{-8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}} = \ln K$$

$$K = 1.25$$

b. The ΔG of formation for the compounds are

$FeCl_3(s)$ = -334.0 J mol^{-1}, $FeCl_2(s)$ = -302.3 J mol^{-1}, Cl(g)=105.3 J mol^{-1}

The calculations are

$$\Delta G_{\text{rxn}} = (-302.3\ \text{J mol}^{-1} + 105.3\ \text{J mol}^{-1}) + 334.0\ \text{J mol}^{-1} = 137\ \text{J mol}^{-1}$$

$$137\ \text{J mol}^{-1} = -8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K} \times \ln K$$

$$\frac{137\ \text{J mol}^{-1}}{-8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}} = \ln K$$

$$K = 0.945$$

c. The ΔG of formation for the compounds are

$CaSO_4(s)$= -1322.0 J/mol, $Ca^{2+}(aq)$ = -553.58 J/mol, $SO_4^{2-}(aq)$ = -744.53 J/mol

The calculations are

$$\Delta G_{\text{rxn}} = (-553.58\ \text{J mol}^{-1} - 744.53\ \text{J mol}^{-1}) + 1322.0\ \text{J mol}^{-1} = 23.89\ \text{J mol}^{-1}$$

$$23.89\ \text{J mol}^{-1} = -8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K} \times \ln K$$

$$\frac{23.89\ \text{J mol}^{-1}}{-8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}} = \ln K$$

$$K = 0.99$$

Q17

To ignite this house on fire, you dowsed the house in some ethanol and used a combustion reaction:

$$\text{C}_2\text{H}_5\text{OH}\,(\text{l}) + \text{O}_2\,(\text{g}) \rightleftharpoons \text{H}_2\text{O}\,(\text{l}) + \text{CO}_2\,(\text{g})$$

This reaction has an equilibrium constant of K_1. If you multiply this equation by 5, will the equilibrium constant change? If so, write this new equilibrium constant, K_2, in terms of K_1.

Solution

Because:

$$K = \frac{[A]^a[B]^b}{[C]^c[D]^d}$$

If we multiply a chemical equation by a constant, the exponents of K will be multiplied by that multiple as well.

For this question, first balance this chemical equation,

$$\text{C}_2\text{H}_5\text{OH}\,(\text{l}) + 3\,\text{O}_2\,(\text{g}) \rightleftharpoons 3\,\text{H}_2\text{O}\,(\text{l}) + 2\,\text{CO}_2\,(\text{g})$$

the corresponding equilibrium constant is

$$K_1 = \frac{[\mathrm{CO_2}]^2}{[\mathrm{O_2}]^3}$$

since liquid is ignored.

When we multiply this equation by 5, the chemical equation becomes,

$$5\,\mathrm{C_2H_5OH\,(l)} + 15\,\mathrm{O_2\,(g)} \rightleftharpoons 15\,\mathrm{H_2O\,(l)} + 10\,\mathrm{CO_2\,(g)}$$

the corresponding equilibrium constant is

$$K_2 = \frac{[\mathrm{CO_2}]^{10}}{[\mathrm{O_2}]^{15}} = \left(\frac{[\mathrm{CO_2}]^2}{[\mathrm{O_2}]^3}\right)^5$$

Therefore, for this reaction, the equilibrium constant changes and $K_2 = K_1^5$.

Q21

An unknown gas B_5D_{10} reacts at room temperature and becomes $B_{10}D_{20}$, the reaction is illustrated with the equation

$$2\,\mathrm{B_5D_{10}\,(g)} \rightleftharpoons \mathrm{B_{10}D_{20}\,(g)}$$

At room temperature the equilibrium partial pressure of B_5D_{10} is 1.23×10^{-4} atm and that of $B_{10}D_{20}$ is 3.14×10^{-16} atm. Given these constants, what is K_p of this reaction at room temperature.

Solution

Given that we already know the partial pressures and this reaction is at equilibrium, we simply substitute the values into the equilibrium equation and solve for Kp.

$$K_p = \frac{[\text{products}]}{[\text{reactants}]}$$

$$K_p = \frac{[3.14 \times 10^{-16}]}{[1.23 \times 10^{-4}]^2} = 2.08 \times 10^{-8}$$

$$K_p = 2.08 \times 10^{-8}$$

Q23A

Suppose there exists a compound that can be found in two forms, red and blue, such that

$$\mathrm{X_{red}} \rightleftharpoons \mathrm{X_{blue}}$$

During equilibrium at 25.0°C, 17% of the substance is determined to be in blue form. What is the equilibrium constant for this reaction?

Solution

The equilibrium constant, $\mathrm{K_{eq}}$, for the chemical equation

$$\mathrm{X_{red}} \rightleftharpoons \mathrm{X_{blue}}$$

can be calculated by constructing the following equation:

$$\mathrm{K_{eq}} = \frac{[\mathrm{X_{blue}}]}{[\mathrm{X_{red}}]}$$

Given that 17% of the concentration is $\mathrm{X_{blue}}$, that means the remaining 83% is $\mathrm{X_{red}}$, which can be plugged into the

equation to yield

$$\mathrm{K_{eq}} = \frac{[0.17]}{[0.83]} = 0.205$$

which can be further reinforced by viewing it as the fact that since $\mathrm{K_{eq}} < 1$, the concentration of products present is expected to be smaller than the concentration of reactants.

Q23B

1,2-dimethylcyclohexane can exist in both boat and chair conformation. There is equilibrium between the two forms. What is the equilibrium constant for the reaction of boat conformation to chair conformation if the molecules in the boat form are 68.7%?

Solution

$$[\mathrm{Boat}] \longrightarrow [\mathrm{Chair}]$$

Let B stand for Boat and C stand for Chair, then the equilibrium constant for this reaction is

$$K = \frac{[\mathrm{C}]}{[\mathrm{B}]}$$

For [C] and [B] here, we can use the molar concentration $c = n/V$, then

$$[\mathrm{C}] = n(\mathrm{C})/V$$
$$[\mathrm{B}] = n(\mathrm{B})/V$$

So

$$K = \frac{n(\mathrm{C})/V}{n(\mathrm{B})/V} = \frac{n(\mathrm{C})}{n(\mathrm{B})} = \frac{n(\mathrm{C})/n_{\mathrm{tot}}}{n(\mathrm{B})/n_{\mathrm{tot}}}$$

From the question, it consists only with boat and chair conformation, so $n(\mathrm{C})/n_{\mathrm{tot}} = 0.687$, and the remaining is for boat, so $n(\mathrm{B})/n_{\mathrm{tot}} = 1 - 0.687 = 0.313$.

Therefore, the equilibrium constant is

$$K = \frac{n(\mathrm{C})/n_{\mathrm{tot}}}{n(\mathrm{B})/n_{\mathrm{tot}}} = \frac{0.687}{0.313} = 2.19$$

Q28

The K_p for the following reaction is 3.0 at 1000 K.

$$\mathrm{CO_2\,(g) + C\,(s) \rightleftharpoons 2\,CO\,(g)}$$

a. If the pressure in the container where the reaction occurs was initially 0.48 bar, calculate the partial pressures of $\mathrm{CO_2}$ and CO at equilibrium.
b. Calculate the percentage of $\mathrm{CO_2}$ that has been dissociated.

Solution

a)

$$\mathrm{CO_2\,(g) + C\,(s) \rightleftharpoons 2\,CO\,(g)}$$

	$\mathrm{CO_2\,(g)}$	$\mathrm{CO\,(g)}$
Initial	0.48	0
Change	$-x$	$+2x$

Equilibrium	$0.48 - x$	$2x$

$$K_p = \frac{p(\mathrm{CO})^2}{p(\mathrm{CO_2})}$$

⇒

$$3 = \frac{(2x)^2}{(0.48 - x)}$$

⇒

$$4x^2 = 3(0.48 - x)$$

⇒

$$4x^2 = 1.44 - 3x$$

⇒

$$4x^2 + 3x - 1.44 = 0$$

By solving the quadratic equation, the positive value we get is

$$x = 0.33$$

Hence at equilibrium,

$$p(\mathrm{CO}) = 2x = 0.66$$

$$p(\mathrm{CO_2}) = 0.48 - x = 0.48 - 0.33 = 0.15\,\mathrm{bar}$$

b) For fraction that has not reacted,

$$\frac{p(\mathrm{CO_2(final)})}{p(\mathrm{CO_2(initial)})} \times 100\%$$

The unreacted percentage is

$$= \frac{0.15}{0.48} \times 100\% = 31.25\%$$

Hence, 68.75% of the CO_2 has reacted.

Q29

A 100.0 mL glass bulb was filled which a weighed sample of solid $\mathrm{XO_3}$, where X is an unknown element. The bulb was then attached to a pressure gauge and heated to 325 K, at which, the pressure was read to be 0.891 atm. Given that all of the $\mathrm{XO_3}$ in the bulb at 325 K was in the gas phase, and it also partially dissociated into $\mathrm{O_2\,(g)}$ and $\mathrm{XO\,(g)}$:

$$\mathrm{XO_3\,(g) \rightleftharpoons O_2\,(g) + XO\,(g)}$$

At 325 K, K_p = 3.14 for this reaction. Calculate the partial pressures of all three species in the bulb at equilibrium.

Solution

$$\mathrm{XO_3\,(g) \rightleftharpoons O_2\,(g) + XO\,(g)}$$

Let Y be the initial partial pressure of X_2O_5, and x is the change in partial pressure of O_2:

ICE	XO_3	O_2	XO
Initial	y	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$y-x$	x	x

The total pressure is 0.891 atm, therefore:

$$(y-x)+x+x=0.891\,\text{atm}$$

$$y+x=0.891\,\text{atm}$$

$$y=0.891-x$$

So the ICE table now would be:

ICE	XO_3	O_2	XO
Initial	$0.891-x$	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.891-2x$	x	x

$$K_p=3.14=\frac{P_{XO}\cdot P_{O_2}}{P_{XO_3}}=\frac{x^2}{0.891-2x}$$

$$x^2+6.28x-2.80=0$$

$$x=0.418$$

$$P_{O_2}=P_{XO}=0.418\,\text{atm}$$

$$P_{XO_3}=0.891-2(0.418)=0.055\,\text{atm}$$

Q31

The equilibrium constant K_c for the reaction

$$\text{F}_2\,(\text{g})+\text{H}_2\,(\text{g})\rightleftharpoons 2\,\text{HF}\,(\text{g})$$

at 298 K is 5.07×10^4. Hydrogen with a partial pressure of 0.03500 atm is mixed with fluorine with a partial pressure of 0.06800 atm, and allowed to reach the equilibrium. What is the partial pressure of each of the gasses at the equilibrium?

Solution

We are looking for partial pressures of the reactants and we have starting partial pressures and a K_c value. First we need to convert K_c to K_p

$$K_p=K_c(RT)^{\Delta n_{\text{gas}}}$$

$$K_p=(5.07\times10^4)\times(0.0821\times298\,\text{K})^0=5.07\times10^4$$

The equilibrium constant can be constructed from the equation given

$$K_p=\frac{[HF]^2}{[H2][F2]}$$

Use an ICE table to find the equilibrium partial pressures of the equilibrium

Reaction	$H_2\,(g)$	$F_2\,(g)$	$2\,HF\,(g)$
I	0.035	0.068	0
C	$-x$	$-x$	$+2x$
E	$0.035 - x$	$0.068 - x$	$2x$

$$5.07 \times 10^4 = \frac{[2x]^2}{[0.035 - x]^2[0.068 - x]^2}$$

Simplify the equation and solve as you wish. You can't use the quadratic formula because you end up with a degree three equation but you can put the equation into a graphing calculator and solve for x using the zero function.

$$x = 0.0286\,\text{atm}$$

$$[HF] = 2x = 0.0571\,\text{atm}$$

$$[H_2] = 0.035 - x = 0.00643\,\text{atm}$$

$$[F_2] = 0.068 - x = 0.0394\,\text{atm}$$

Q33

At 25 °C, the equilibrium constant for the reaction below has the value of 1.7×10^{-13}:

$$N_2O\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightleftharpoons 2\,NO\,(g)$$

In a container where N_2O has an initial partial pressure of 0.62 atm, O_2 has a pressure of 0.24 atm, and NO has an initial pressure of 0.08 atm, what will the partial pressure of the three gases be after reaching equilibrium at the same temperature?

Q35

The reaction:

$$2\,HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$$

has an equilibrium constant $K_c = 1.82 \times 10^{-2}$ at 698 K. If the reaction took place in a tank at 698 K and started off with HI having a partial pressure of 1 atm, what would the partial pressures of all the gases be at equilibrium?

Solution

First, we need to convert K_c into K_p with the equation

$$K_p = K_c(RT)^{\Delta n}$$

$$K_p = 1.82 \times 10^{-2}(0.0821\,\text{L atm / K mol} \times 698\,\text{K})^{2-2}$$

$$K_p = 1.82 \times 10^{-2}$$

An ICE table can also be constructed for the reaction:

$$2\,HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$$

ICE Table	$2\,HI\,(g)$	$H_2\,(g)$	$I_2\,(g)$
Initial	1	0	0

ICE Table	$2\,\mathrm{HI(g)}$	$\mathrm{H_2(g)}$	$\mathrm{I_2(g)}$
Change	$-2x$	$+x$	$+x$
Equilibrium	$1-2x$	x	x

$$0.82 \times 10^{-2} = \frac{x^2}{1-2x}$$

$$x^2 = 1.82 \times 10^{-2} - 0.0368x$$

$$x = 0.118488$$

$$\text{partial pressure of HI} = 0.763\,\text{atm}$$

$$\text{partial pressure of } \mathrm{H_2} = \text{partial pressure of } \mathrm{I_2} = 0.1189\,\text{atm}$$

Q37

What is the concentration of a XY that will be found in equilibrium at room temperature, given that $\mathrm{X_2}$ has a concentration of 3.14×10^{-15} M, $\mathrm{Y_2}$ has a concentration of 1.23×10^{-4} M, and the K_c of the reaction is 2.22×10^{-7} M.

Solution

First we must state what the formulas for both the reaction and K_c and then we can substitute the known values and solve for the concentration of XY as an unknown variable.

$$2\,\mathrm{XY(g)} \rightleftharpoons \mathrm{X_2(g)} + \mathrm{Y_2(g)}$$

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$K_c = \frac{[X2][Y2]}{[XY]^2} = \frac{[3.14 \times 10^{-15}][1.23 \times 10^{-4}]}{[\mathrm{XY}]^2} = 2.22 \times 10^{-7}$$

$$K_c = \frac{[3.86 \times 10^{-19}]}{[\mathrm{XY}]^2} = 2.22 \times 10^{-7}$$

$$K_c = 3.86 \times 10^{-19} = 2.22 \times 10^{-7}[\mathrm{XY}]^2$$

$$[\mathrm{XY}] = 1.32 \times 10^{-6}$$

So the concentration of XY is 1.32×10^{-6} M in equilibrium at 25°C.

Q41

Hydrogen and oxygen gas react with each other to form gaseous water with an equilibrium constant for the reaction is $K_c = 1.33 \times 10^{20}$ at 1000 K.

a. Consider a system at 1000.0 K in which 4.00 atm of oxygen is mixed with 0.500 atm of hydrogen and no water is initially present. What is the concentration of hydrogen gas after equilibration.
b. Consider a system, also at 1000.0 K, where 0.250 atm of oxygen is mixed with 0.500 atm of hydrogen and 2.000 atm of water. What is the concentration of hydrogen and oxygen gas after equilibration.

Solution

a)

$$2\,H_2\,(g) + O_2\,(g) \rightleftharpoons 2\,H_2O\,(l)$$

$$K = 3.4 = \frac{1}{P_{H_2}^2 P_{O_2}}$$

$$P_{H_2} = 1.2\,\text{atm}$$

$$3.4 = \frac{1}{(1.2)^2 P_{O_2}}$$

$$P_{O_2} = \frac{1}{(1.2)^2(3.4)} = 0.204\,\text{atm}$$

b) Excess $H_2O\,(l)$ is added drive the reaction to the left towards the reactant to reach the equilibrium; therefore, pressure of H_2 and O_2 increased.

	$2\,H_2\,(g)$	$O_2\,(g)$	$2\,H_2O\,(l)$
Initial	0	0.3	N/A
Change	$+2x$	$+x$	N/A
Equilibrium	$2x$	$0.3 + x$	N/A

$$K = \frac{1}{(2x)^2(0.3 + x)} = 3.4$$

$$3.4(0.3 + x)(2x)^2 = 1$$

$$x = 0.339\,\text{atm}$$

$$P_{O_2} = 0.3 + 0.339 = 0.639\,\text{atm}$$

$$P_{H_2} = 2(0.339) = 0.678\,\text{atm}$$

Q43

If you decompose ammonium nitrate into water and nitrous oxide, which further decomposes into oxygen and nitrogen gas, making the final reaction:

$$2\,NH_4NO_3\,(s) \rightleftharpoons 2\,N_2\,(g) + O_2\,(g) + 4\,H_2O\,(g)$$

This reaction takes place only in the molten salt, above its melting point of 169.6°C (for the anhydrous product). So, you get your 170°C blow torch and begin decomposing the ammonium nitrate under a sealed hood. Upon decomposition, all of the ammonium nitrate is gone, i.e. the reaction goes to completion.

a. What can be said of the equilibrium constant of this reaction at 170°C?
b. Now, in another universe, the partial pressure of N_2(g) is 0.3 atm initially. Will the reaction still go to, essentially, completion?

Solution

(a) If there is no ammonium nitrate left, then the reaction was **heavily** products favoring, meaning K is extremely high at 170°C.

Note: It's more accurate to say that Q is a big number when there is no reactants left after reaction occurred. Reviewer's comment: Q stands for the current state. K is the equilibrium constant. When there is no reactant left after reaction occurred, the reaction is at the equilibrium state, so Q = K. Since Q is a big number, then K is also a big number.

(b) There would have to be an enormous amount of Nitrogen to force the reaction backwards. Because 0.3 atm is likely not enough to push back an essentially irreversible reaction, it has no noticeable affect on the amount of end product. (Note: If the reactants and products are essentially gas, we calculate the equilibrium constant not by its concentration, but by its pressure.)

Q45

Al_2Cl_6 at a partial pressure of 0.600 atm is placed in a closed container at 454 K. Al_3Cl_9 (partial pressure 1.98×10^{-3} atm) is also placed in it as well. Argon is added to raise the total pressure up to 1.00 atm.

Find whether if there is going to be net production or consumption of Al_3Cl_9 given $K_p = 1.04 \times 10^{-4}$. Then find the final pressure of Al_3Cl_9.

Solution

The reaction is

$$3\,\mathrm{Al_2Cl_6\,(g)} \rightleftharpoons 2\,\mathrm{Al_3Cl_9\,(g)}$$

Because argon does not react, it can be ignored.

$$Q = \frac{([\mathrm{Al_3Cl_9}])^2}{([\mathrm{Al_2Cl_6}])^3} = \frac{(1.98 \cdot 10^{-3})^2}{(0.600)^3} = 1.82 \cdot 10^{-5} < K_p = 1.04 \cdot 10^{-4}$$

There will be production of Al_3Cl_9.

ICE Table	Al_2Cl_6	Al_3Cl_9
Initial	0.600	1.98×10^{-3}
Change	$-3y$	$+2y$
Equilibrium	$0.6 - 3y$	$1.98 \times 10^{-3} + 2y$

$$K = 1.04 \cdot 10^{-4} \frac{([\mathrm{Al_3Cl_9}])^2}{([\mathrm{Al_2Cl_6}])^3} = \frac{(1.98 \times 10^{-3} + 2y)^2}{(1 - (1.98 \times 10^{-3} + 2y))^3}$$

Solving out

$$y = 0.0041\,\mathrm{atm}$$

Al_3Cl_9 final pressure = 0.0102 atm.

Q46

The thermal decomposition of NH_4Cl solid proceeds as follows:

$$\mathrm{NH_4Cl\,(s)} \rightleftharpoons \mathrm{NH_3\,(g)} + \mathrm{HCl\,(g)}$$

the equilibrium constant at 275°C is 1.04×10^{-2}. If the partial pressures of $\mathrm{NH_3\,(g)}$ and $\mathrm{HCl\,(g)}$ are equal, and the total partial pressure of the system is 0.200 atm, in what direction does the reaction proceed? What will be formed?

Solution

First, we make two equations to solve out the partial pressures. To get the first equation, we sum over the partial pressures to the total pressure. $\mathrm{NH_4Cl}$ is a solid, so it doesn't contribute to the partial pressure

$$P_{\mathrm{NH_3}} + P_{\mathrm{HCl}} = 0.200\,\mathrm{atm}$$

The second equation is from the question that partial pressures of $\mathrm{NH_3\,(g)}$ and $\mathrm{HCl\,(g)}$ are equal

$$P_{NH_3} = P_{HCl}$$

Hence,

$$P_{NH_3} = P_{HCl} = 0.100\,\text{atm}$$

$$Q(\text{reaction quotient}) = P_{NH_3}P_{HCl} = (0.100)^2$$

$$10^{-2} < 1.04 \times 10^{-2}$$

$$Q < K$$

Hence, the reaction will slightly proceed more in the forward direction.

NH_3 and HCl will be formed.

Q47

A tube contains a mixture of NO_2 and N_2O_4 gas is set at 298K, in which the initial partial pressure NO_2 is 0.38 atm, and the initial partial pressure of N_2O_4 is 0.59 atm. NO_2 is a brownish gas, while N_2O_4 is a colorless gas.

$$2\,NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$$

a. What is the reaction quotient at the start of this reaction?
b. As the reaction shown above reaches equilibrium, the mixture becomes more brown. With this in mind, is the equilibrium constant, K_p, greater than or less than the Q calculated in part a?

Solution

a)

$$2\,NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$$

$$P_{N_2O_4} = 0.59\text{ atm} \quad P_{NO_2} = 0.38\text{ atm}$$

$$Q_p = \frac{P_{N_2O_4}}{(P_{NO_2})^2}$$

$$Q_p = \frac{0.59}{0.38^2} = 4.1$$

b) Since the mixture becomes more brown as the reaction reaches equilibrium, more NO gas is being produced, therefore the reverse reaction is favored, so $Q_p > k_p$, in conclusion, $K_p < 4.1$.

Q49

At 500 K the equilibrium constant for the reaction:

$$PCl_3\,(g) + Cl_2\,(g) \rightleftharpoons PCl_5\,(g)$$

is $K_{eq} = 2.1$. Suppose the equilibrium is disturbed and shifts, while temperature remains constant. Calculate the reaction quotient for each one of the possible changes in equilibrium concentration given below and evaluate in what direction the reaction will shift to reestablish equilibrium.

a. [PCl_3]= 0.0563, [Cl2]= 0.0784, [PCl_5]= 0.8934.
b. [PCl_3]=0.4390 , [Cl2]= 0.3547, [PCl_5]= 0.1048.
c. [PCl_3]= 0.4018, [Cl2]= 0.8690, [PCl_5]= 0.7205.

Q48

NO_2 has a brownish color. At elevated temperatures, NO_2 reacts with CO

$$\mathrm{NO_2\,(g) + CO\,(g) \rightleftharpoons NO\,(g) + CO_2\,(g)}$$

The other gases in this equation are colorless. When a gas mixture is prepared at 600K, in which 9.6 atm is the initial partial pressure of both NO_2 and CO, and 5.4 atm is the partial pressure of both NO and CO_2, the brown color of the mixture observed begins to get stronger as the reaction progresses toward equilibrium. Give a condition that must be satisfied by the equilibrium constant K.

Q51

The equilibrium constant (K_p) for the reaction

$$\mathrm{As_4\,(g) \rightleftharpoons 2\,As_2\,(g)}$$

is 5.5837×10^{-4} at 1090 K.

a. The initial molarity of $[\mathrm{As_4}]$ is 2.3 M and the initial molarity of $[\mathrm{As_2}]$ is 0.001 M. Calculate the reaction quotient Q and determine which way the reaction proceeds.
b. Calculate the molarity of each compound at the equilibrium.
c. Which direction will the reaction proceed if the pressure on the reaction decreases? Explain your answer.

Solution

(a) First, because you are given the initial molarities of your products and reactants and a Kp instead of a Kc value, you have to convert Kp to Kc using the formula:

$$K_p = K_c(RT)^{\Delta n_{\text{gas}}}$$

Plug in your given values

$$5.5837 \times 10^{-4} = K_c(0.0821 \times 1090)^{2-1} = 89.489K_c$$

$$K_c = 6.24 \times 10^{-6}$$

Set up a reaction quotient for the equation given

$$Q = \frac{[\mathrm{As_2}]^2}{[\mathrm{As_4}]} = \frac{[0.001]^2}{[2.3]} = 4.35 \times 10^{-7}$$

Reaction will progress towards the right to reach equilibrium

(b) Set up an ice chart to find the equilibrium molarities

Reaction	P_4	2 P_2
I	2.3	0.001
C	$-x$	$+2x$
E	$2.3 - x$	$0.001 + 2x$

$$6.24 \times 10^{-6} = \frac{[0.001 + 2x]^2}{[2.3 - x]}$$

$$4x^2 + 0.00400624x - 1.3352 \times 10^{-5} = 0$$

Use the quadratic equation to find x

$$x = -0.0024, 0.00139$$

-0.0024 is negative, which can't happen in real life so we know \(x) actually equals 0.00139.

[P_4]= 2.29861 M

[P_2]= 0.00378 M

(c) The reaction will progress towards the right because as pressure decreases, the reaction moves towards the side with the most moles of gas, which is the products.

Q55

Consider a reaction involving only gaseous compounds. The product yield at equilibrium decreases when the temperature and volume increase.

a. Is this reaction endothermic or exothermic?
b. Does the number of gas molecules in this reaction increase or decrease?

Solution

a. Exothermic. In exothermic reactions, product yield is indirectly related to temperature. In endothermic reactions, product yield is directly related to temperature. These properties can be further explained when heat is thought of as a reactant or a product. In exothermic reactions, heat is a product, and in endothermic reactions, heat is a reactant. When heat is added to a reaction, the equilibrium shifts to the opposite side to relieve stress on the system.

b. Decreases. The number of gas molecules is directly related to the volume of the container in which the reaction is happening. For example, if the volume of the container is decreased, the reaction will shift to whichever side has fewer moles of gas.

Q57

the Haber process, also called the Haber–Bosch process, is an artificial nitrogen fixation process and is the main industrial procedure for the production of ammonia today.

$$\mathrm{N_3 + 3\,H_2 \rightleftharpoons 2\,NH_3} \quad (\Delta H = -92.4\,\mathrm{kJ/mol})$$

Determine the best condition of temperature and pressure to yield the most ammonia.

Solution

Because Haber process is an exothermic reaction, a lower temperature will maximize the yield of product. Also, according to the ideal gas law, because the moles of gas are proportional to the volume, and the volume is inverse proportional to the pressure; a higher pressure is required to maximize the yield of product.

Q59

At room temperature, a vessel is filled with gaseous carbon dioxide. Some water is added at 2.00 atm. It is well-shaken, integrating carbon dioxide gas into the water. 0.5 kg of the solution is taken out and boiled to extract 2.50 L of carbon dioxide. The system is at 10 degree Celsius and 1.00 atm. What is the Henry's Law constant for carbon dioxide in water?

Solution

given that the extracted solution:

$$PV = nRT \tag{5.E.1610}$$

$$n = \frac{PV}{RT} = \frac{1\,\text{atm} \times 2.5\,\text{L}}{0.082\,\frac{\text{L atm}}{\text{mol K}} \times 283.15\,\text{L}} = 0.1077\,\text{mol} \tag{5.E.1611}$$

$$m_{CO_2} = n_{CO_2} \times \text{molar mass} = 0.1077\,\text{mol} \times 44\,\text{g/mol} = 4.7388\,\text{g} \tag{5.E.1612}$$

$$m_{H_2O} = 500\,\text{g} - 4.7388\,\text{g} = 495.29\,\text{g} \tag{5.E.1613}$$

$$n_{H_2O} = \frac{495.29\,\text{g}}{18\,\text{g/mol}} = 27.5\,\text{mol} \tag{5.E.1614}$$

[redacted]

Due to the Ideal gas law, the ratio of moles equals to the ratio of pressure

pressure: pressure = mol:mol = 0.1077: 27.51

because the total pressure is 2 atm, partial pressure of CO_2 = 0.0724 atm

Due to Henry's law:

$$k = \frac{c}{P} = \frac{0.2154 mol/kg}{0.0724\ atm} = 2.9751 \frac{mol}{kg\ atm} \tag{5.E.1615}$$

Q61

The equilibrium constant for a reaction increases from $\mathrm{K}= 4.5\ \times 10^{-2}$ to $\mathrm{K}= 4.5$ as the temperature increases from $0.00°\mathrm{C}$ to $300.0°\mathrm{C}$. Assuming the change in enthalpy ($\Delta\mathrm{H}$) and change in entropy ($\Delta\mathrm{S}$) are constant over this range of temperatures, what is $\Delta\mathrm{S}$ for this reaction? Is this reaction endothermic or exothermic?

Solution

Assuming $\Delta\mathrm{H}$ and $\Delta\mathrm{S}$ are constant, we can set up a system of equations as follows:

$$\begin{cases} \Delta G_{0.00°\mathrm{C}} = \Delta\mathrm{H} - \mathrm{T}\Delta\mathrm{S} \\ \Delta G_{300.0°\mathrm{C}} = \Delta\mathrm{H} - \mathrm{T}\Delta\mathrm{S} \end{cases}$$

We can determine $\Delta G_{0.00°\mathrm{C}}$ and $\Delta G_{300.0°\mathrm{C}}$ by utilizing the equation below that relates ΔG to $\mathrm{K_{eq}}$:

$\Delta G = -\mathrm{RT}\ \ln(\mathrm{K})$ Easily remembered using the mnemonic: "ΔGet in the $-$RighT lane, K?"

$$\Delta G_{0.00°\mathrm{C}} = -\left(8.314\,\tfrac{\mathrm{J}}{\mathrm{K\times mol}}\right)(273.15\mathrm{K})\left(\ln(4.5\times10^{-2})\right) = 7042.5\,\tfrac{\mathrm{J}}{\mathrm{mol}}$$

$$\Delta G_{300.0°\mathrm{C}} = -\left(8.314\,\tfrac{\mathrm{J}}{\mathrm{K\times mol}}\right)(573.15\mathrm{K})\left(\ln(4.5)\right) = -7167.2\,\tfrac{\mathrm{J}}{\mathrm{mol}}$$

These values can then be plugged back into the original system of equations to obtain

$$\begin{cases} \Delta G_{0.00°\mathrm{C}} = 7042.5\,\tfrac{\mathrm{J}}{\mathrm{mol}} = \Delta\mathrm{H} - (273.15\mathrm{K})\,\Delta\mathrm{S} \\ \Delta G_{300.0°\mathrm{C}} = -7167.2\,\tfrac{\mathrm{J}}{\mathrm{mol}} = \Delta\mathrm{H} - (573.15\mathrm{K})\,\Delta\mathrm{S} \end{cases}$$

To calculate the values of the remaining two unknown variables, a substitution can be made that expresses $\Delta\mathrm{H}$ in terms of $\Delta\mathrm{S}$.

$$-7167.2\,\tfrac{\mathrm{J}}{\mathrm{mol}} + (573.15\mathrm{K})\,\Delta\mathrm{S} = \Delta\mathrm{H}$$

This substitution can be plugged into the first equation to calculate the value for $\Delta\mathrm{S}$.

$$7042.5\,\tfrac{\mathrm{J}}{\mathrm{mol}} = -7167.2\,\tfrac{\mathrm{J}}{\mathrm{mol}} + (573.15\mathrm{K})\,\Delta\mathrm{S} - (273.15\mathrm{K})\,\Delta\mathrm{S}$$

$$\Delta\mathrm{S} = 47.37\,\tfrac{\mathrm{J}}{\mathrm{K\times mol}}$$

ΔH can be calculated now by plugging in the value for ΔS into either one of the equations in the original set.

$$7042.5\frac{\text{J}}{\text{mol}} = \Delta\text{H} - (273.15\text{K})\left(47.37\frac{\text{J}}{\text{K}\times\text{mol}}\right)$$

$$\Delta\text{H} = 19980\frac{\text{J}}{\text{mol}} = 19.98\frac{\text{kJ}}{\text{mol}}$$

Because ΔH is positive, we know the reaction is endothermic.

Q63A

The equilibrium constant for the reaction $\text{N}_2\text{O}_4\,(\text{g}) \rightleftharpoons 2\,\text{NO}_2\,(\text{g})$ is measured to be 5.9×10^{-3} at 298\;K and 1.3×10^{-6} at $398\ \ K$

a. Calculate ΔG° at 298 K for the reaction.
b. Calculate ΔH and ΔS°, assuming the enthalpy and entropy changes are independent of temperature between 298 K and 398 K.

Solution

a.Use the equation $\Delta G^\circ = -RT\ln K$

$$\Delta G^\circ = -RT\ln K = (-8.3145\ \ \text{J}\,\text{K}\,\text{mol}^{-1}) \times (298\ \ \text{K})(\ln 5.9 \times 10^{-3}) = -1.29 \times 10^4\ \ \text{J}\,\text{mol}^{-1}$$

For one mole of the reaction as written, ΔG° is -1290 kJ.

b. Use van't Hoff equation and the values of K at 298 K and at 398 K to obtain ΔH°. Then get ΔS° from ΔG° and the equation $\Delta G^\circ = -RT\ln K$

$$\ln\left(\frac{1.3\times10^{-6}}{5.9\times10^{-3}}\right) = \frac{\Delta H^\circ}{8.3145\ \text{J}\,\text{K}^{-1}\,\text{mol}^{-1}}\left(\frac{1}{398\ K} - \frac{1}{298\ K}\right)$$

$$\Delta\ H^\circ = 83.0\ \ kJ$$

The answer equals both $\Delta\ H^\circ$ at 298 K and 398 K because it is assumed in the derivation of the van't Hoff equation that $\Delta\ H^\circ$ is independent of temperature. Next,

$$\Delta\ S^\circ = \frac{\Delta\ H^\circ - \Delta\ G^\circ}{T} = \frac{83.0\times10^3\ J-(-1.29\times10^4\ J)}{298\ K} = 323\ \ J\ \ K^{-1}$$

Q63B

For the reaction: $\text{Br}_2\,(\text{g}) \rightleftharpoons 2\,\text{Br}\,(\text{g})$, the equilibrium constant is 4.64×10^{-29} at 25°C and 1.1×10^{-3} at 1280 K.

a. What is ΔG of the reaction at 298 K?
b. Assuming that ΔH^o and ΔS^o are independent of temperature, what are the values of enthalpy and entropy when the temperature changes to 1280 K?

Solution

a. ΔG = RTln(k)

= $(8.3145\text{JK}^{-1}\text{mol}^{-1})(298\text{K})\ln(4.64\text{x}10^{-29})$

= -161.65kJ

a)

$$ln\left(\frac{1.1x10^{-3}}{4.64x10^{-29}}\right) = \frac{-\Delta H}{R}\left(\frac{1}{1280K} - \frac{1}{298K}\right)$$

Solve for Δ H.

Δ H = 188.70 KJ

$$ln\,(k) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

\[ln \left({1.1x10^{-3}}\right) = \dfrac{-188699.30}{(8.3245;\ {JK^{-1}mol^{-1}})(1280:\K} + \dfrac{ ΔS}{R} \nonumber \]

ΔS =90.78 $JK^{-1}mol^{-1}$

Q65

Calculate the equilibrium constant for the reaction,

$$2\ NO_2\ (g) \rightleftharpoons N_2O_4\ (g) \text{ at } 500\ K,$$

given the equilibrium constant K = 4.65 x 10^{-3} at 298 K, and ΔH° = -57.2 kJ mol^{-1}. Assume that ΔH° does not change between 298 K and 500 K

Solution

Use the van 't Hoff equation to calculate K_{500} from K_{298} and the standard enthalpy of the reaction ΔH°:

$$ln\frac{K_{500}}{K_{298}} = -\frac{\Delta H°}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$

=> K_{500} = 3.366 x 10^{-7}

Solve for the unknown variable, in this case it is K_{500}. T_1 is equal to 298K while T_2 is equal to 500K.

Q69

The equilibrium constant for the following reaction was experientially calculated at different temperatures.

$$\mathrm{N_2\,(g) + 3\,H_2\,(g)\ \rightleftharpoons 2\,NH_3\,(g)}$$

Temperature (°C)	300	400	450	500	550	600
Equilibrium Constant (K_{eq})	4.34 x 10^{-3}	1.64 x 10^{-4}	4.51 x 10^{-5}	1.45 x 10^{-5}	5.38 x 10^{-6}	2.25 x 10^{-6}

a. Plot $\ln K$ as a function of $1/T$ (K^{-1})
b. What is ΔH° of the equilibrium reaction with ammonia? HINT: use the slope to find the ΔH°

Solution

The graph bellow shows what the graph should look like:

First we must write the van't Hoff equation:

[redacted]

Writing the equation like this how it can be compared with y = mx + b. With this information we then know that the slope of the graphe is equal to -ΔH^{o}/R. So:

ΔH^{o} = -mR were R = 8.3145 J $K^{-1}mol^{-1}$

ΔH^o = -104.9 kJ mol^{-1}

Q71

At a certain temperature, $0.5\ \text{mol}\ \text{I}_{2\ (\text{aq})}$ is dissolved in $2\ \text{L}\ \text{H}_2\text{O}$ and shaken vigorously in a container with $2\ \text{L}$ of CCl_4, an immiscible liquid. The container is then left to equilibrate during which time the iodine redistributes itself between the layers of H_2O and CCl_4 as indicated by the following reaction:

$$\text{I}_{2\ (\text{aq})} \rightleftharpoons \text{I}_2\ (\text{CCl}_4)$$

The final concentration of $\text{I}_{2\ (\text{aq})}$ is determined to be $0.0710\ \text{M}$. What is the partition coefficient (K) for this process?

Solution

The word "equilibrate" is a dead giveaway for "ICE Table" so we can establish the following ICE Table based on the information provided for the reaction provided.

$\text{I}_{2\ (\text{aq})} \rightleftharpoons \text{I}_2\ (\text{CCl}_4)$

ICE Table	$\text{I}_{2\ (\text{aq})}$	$\text{I}_2\ (\text{CCl}_4)$
Initial	0.250M	0M
Change	$-\text{x}$	$+\text{x}$
Equilibrium	0.0710M	$+\text{x}$

x can be calculated by solving the following equation:

$$0.250\text{M} - \text{x} = 0.0710\text{M}$$

$$\text{x} = 0.179\text{M}$$

This value can then be plugged into the ICE Table to obtain equilibrium values for $\text{I}_{2\ (\text{aq})}$ and $\text{I}_2\ (\text{CCl}_4)$. (Remember that the two liquids are immiscible so the molarity isn't 0.125M as $\text{I}_2\ (\text{CCl}_4)$ does not contribute to the initial molarity of the solution.)

ICE Table	$\text{I}_{2\ (\text{aq})}$	$\text{I}_2\ (\text{CCl}_4)$
Initial	0.250M	0M
Change	-0.179M	$+0.179\text{M}$
Equilibrium	0.0710M	$+0.179\text{M}$

The equilibrium concentrations of $\text{I}_{2\ (\text{aq})}$ and $\text{I}_2\ (\text{CCl}_4)$ can then be plugged into the equilibrium constant expression and solve for the partition coefficient.

$$\text{K} = \frac{0.179\text{M}}{0.0710\text{M}}$$

$$\text{K} = 2.52$$

Q73

At 25°C, 0.130 g/L of chloroacetic acid ($C_2H_3ClO_2$) dissolve in of water, and at the same temperature 0.2834 g/L of chloroacetic acid dissolve in 1-octanol.

a. Calculate the following equilibrium constants

$$C_2H_2ClO_2H\,(s) \rightleftharpoons C_2H_2ClO_2H_{(aq)}$$

$$C_2H_2ClO_2H\,(s) \rightleftharpoons C_2H_2ClO_2H_{(octanol)}$$

b. Calculate the *participation coefficient*, K, of the combined reactions.

$$C_2H_2ClO_2H\,(aq) \rightleftharpoons C_2H_2ClO_2H_{(octanol)}$$

Solution

First, we will need g/L to M so that we can calculate the equilibrium constant.

$$\left(\frac{0.130\ \cancel{g\ C_2H_3ClO_2}}{1\ L}\right)\left(\frac{1\ mol}{94.494\ \cancel{g\ C_2H_3ClO_2}}\right) = 0.0013757\ M$$

$$\left(\frac{0.2834\ \cancel{g\ C_2H_3ClO_2}}{1\ L}\right)\left(\frac{1\ mol}{94.494\ \cancel{g\ C_2H_3ClO_2}}\right) = 3.00x10^{-3}\ M$$

$$K = \frac{K_{forminde}}{K_{aq}} = \frac{3.00 \times 10^{-3}}{0.001376} = 2.18$$

$$\log_{10} K_{oct/wat} = 0.338$$

Q75

At 298 K, the two gases NOBr and Br_2 have the number of moles of 1.25 and 8.5 x 10^{-5} at equilibrium with a sufficient amount of solid NO. Determine the equilibrium constant of the reaction:

$$2NOBr_{(g)} \rightleftharpoons 2NO_{(s)} + Br_{2(g)}$$

Solution

Use: $P_{gas} = n_{gas}(RT/V)$

$K = P_{Br2} / P^2_{NOBr} = n_{Br2} / n^2_{NOBr} = 5.44 \times 10^{-5}$

The volume is needed to solve this problem. It is necessary to find the value of K regardless of it is K_p or K_c.

Q79

At 300 K and 1 atm, N_2O_4 is partly dissociated into NO_2. The density of the equilibrium mixture was 2.076 g/L. What is the degree of dissociation of N_2O_4 under these circumstances?

Solution

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

moles of N_2O_4 at equilibrium = 1-x moles of NO_2 at equilibrium = 2x

Therefore, the degree of dissociation of SO_3 is 0.8.

(Multiplying number of moles by molar mass to get the total mass)

92*(1- x) + [46*(2x)/ (1+x)]= [2.076 g/L * 0.08206 (L*atm)/(mol*K)] / 1 atm

On solving the equation, we get the equation, x= 0.8

Q85

The decompressions of calcium carbonate ($\mathrm{CaCO_3}$) occurs according to the following reaction:

$$\mathrm{CaCO_3\,(s)} \rightleftharpoons \mathrm{CaO\,(s) + CO_2\,(g)}$$

100 g of solid calcium carbonate ($\mathrm{CaCO_3}$) and 50 g of calcium oxide (CaO) are placed in an evacuated round bottom flask that is heated up to 35°C. At this temperature the pressure in the round bottom flask is found to be 0.5 atm.

a. What is the equilibrium constant of the decompressions of calcium carbonate ($\mathrm{CaCO_3}$) at 35°C?
b. If 100 g of calcium oxide (CaO) at 35°C was added to the flask what would be the new total pressure of the flask and why?
c. If the pressure in the round bottom flask would to increase to 1.0 atm, then what would would be the new equilibrium constant?

Solution

a. First we need to write the equilibrium expression for the reaction:

$$K_{eq} = p\mathrm{CO_2}] \tag{5.E.1616}$$

Now we just need to plug in the pressure of CO_2: K_{eq} = [0.5] = 0.5

b. The total pressure would still be 0.5 atm because solids have an activity of 1 so they don't effect the equilibrium pressure.
c. The new equilibrium constant would be 1.0 atm.

Q87

Let's say you have the reaction:

$$A(s) + B(g) \leftrightharpoons C(s) + D(g)$$

At 25°C, this reaction has an equilibrium constant of 157.2. Find the partial pressures of $B(g)$ and $D(g)$ when the total pressure of the system is equal to 4.3 atm.

Solution

First, the equilibrium expression of this reaction is

$$K_c = \frac{D(g)}{B(g)} = 157.2$$

Note, the A(s) and C(s) are not included in this expression because they are solids. Solids have an activity equal to 1 which basically means they do not affect the equilibrium of the reaction.

To calculate the partial pressure of our unknowns, we can use Dalton's Law of partial pressures:

$$P_A = X_A P_{Total}$$

Since we are looking for the partial pressure of each of our gases, and we already have the total pressure of the system, we need to find the mole fraction of each of our gases. To find it, we can manipulate the above equilibrium expression to get:

$$D(g) = 157.2\ B(g)$$

Here, we see that at equilibrium, there are 157.2 molecules of $D(g)$ for every 1 molecule of $B(g)$

Now that we have the ratio of molecules in this reaction, we can construct workable mole fractions.

$$X_D = \frac{157.2}{1+157.2}$$

$$X_B = \frac{1}{1+157.2}$$

Finally, we can plug everything in to find our partial pressures.

$$P_D = \frac{157.2}{158.2} \times (4.3\ \ atm) = 4.27\ \ atm$$

$$P_B = \frac{1}{157.8} \times (4.3\ \ atm) = 0.027\ \ atm$$

Q91

Given the reaction

$$C_3H_5N(g) + 3\ H_2(g) \leftrightharpoons C_5H_{11}N(g)$$

whose equilibrium constant is solved by this equation

$$log_{10}(K) = -20.28 + \frac{10.56\ K}{T}$$

a. Solve for K when $T = 200\ \ K$
b. What is partial pressure of $C_3H_5N(g)$ when $T = 200\ \ K$ and the partial pressure of hydrogen is 1.0 atm and the partial pressure of $C_5H_{11}N(g)$ is 2.0×10^{-5} atm.

Solution

Part a)

$$log_{10}(K) = -20.28 + \frac{10.56\ K}{200\ K}$$

$$K = 10^{-20.23} = 5.89 \times 10^{-21}$$

part b)

Set up the equilibrium constant of the reaction, plug in your partial pressures, and solve for $C_3H_5N(g)$

$$K = \frac{[C_5H_{11}N]}{[C_5H_5N]\ [H_2]^3}$$

$$K = \frac{2.0 \times 10^{-5}}{[C_5H_5N]\ [1]}$$

$$[C_5H_5N] = 3.40 \times 10^{15}$$

Q93

Two equal volume solutions of 2M $HCOO^-$ and 2M HCOOH are mixed together. Assume that the volumes are additive. The value of the equilibrium constant Ka for HCOOH is 1.77 x 10^{-4}. What is the ratio between the amounts of HCOOH and $HCOO^-$ in the solution at equilibrium?

Solution

The chemical equation for this reaction is

$$HCOOH_{(aq)} + H_2O_l \leftrightarrow H_3O^+_{(aq)} + HCOO^-_{(aq)}$$

This indicates that

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

Because the volumes are equal and additive, the concentrations of the two solutions become half of what they were initially.

At equilibrium,

$$[HCOO^-] = 1 + x$$

$$[H_3O^+] = x$$

$$[HCOOH] = 1 - x$$

Plugging in these values into the equilibrium expression gives

$$1.77 \bullet 10^{-4} = \frac{[1+x][x]}{[1-x]}$$

Solving the equation for x gives

$$x = 1.77 \bullet 10^{-4} M$$

The ratio of HCOOH and $HCOO^-$ is

$$\frac{1+x}{1-x}$$

and due to x being such a small value, the ratio between the amounts of HCOOH and $HCOO^-$ is essentially 1.

Q101

The \(ΔG_f^o\) of $\mathrm{PbO\,(s)}$ is -188.95 kJ mol^{-1}. Calculate the equilibrium pressure of O_2(g) over a sample of pure PbO(s) in contact with pure Pb(s) at 25°C. PbO(s) decomposes according to the equation

$$\mathrm{PbO_{(s)} \rightleftharpoons Pb\,(s) + \tfrac{1}{2}\,O_2\,(g)}$$

Solution

Since $G_f°$ for O_2(g) and Pb_s(s) is 0, for the reaction

$$\Delta G^\circ = (0+0) - (-188.95 kJ mol^{-1}) = 188.95 kJ mol^{-1}$$

The equilibrium constant of the reaction can be computed by

$$lnK = -\frac{\Delta G^\circ}{RT} = -76.22$$

$$K = 7.898 \bullet 10^{-34}$$

From the chemical equation, we can tell

$$K = (P_{O_2})^{1/2}$$

Therefore the equilibrium pressure of O_2 at 25°C

$$P_{O_2} = 6.2 \bullet 10^{-67} atm$$

Q105

If that weren't enough, Jim's sister, ., knocked his grass juice (a mixture of 1-Hexanol, Cl_2, $CaCl_2$, and cyclohexane) into the family's benzene-ethanol vat! Assume that the two solvents in the vat are immiscible with each other but are miscible with the grass juice components. Jim separates the benzene and ethanol, and drinks the one with the greater amount of 1-Hexanol. Which one does he drink? Which of the two solvents have the highest concentration of the other components of the grass juice?

Solution

There are two immiscible solvents in the family vat. What this means is that they do not mix/ dissolve well in each other. Consequently, when . poured the grass juice into this vat, the solution technically contains two solvents. Evidently, what

this means is that each of the solutes (which are the grass juice constituents mentioned in the question) dissolves to a different extent in each solvent. When the question asks which solvent has the greater amount of 1-Hexanol, it is the same as asking does 1-Hexanol dissolve “more” in either benzene or ethanol (the two solvents). The concept of “like dissolves like” is very important here, and to solve this problem first benzene must be identified as non-polar and driven by dispersion forces, while ethanol is polar. Since polar solvents dissolve polar solutes, then ethanol should be able to dissolve $CaCl_2$ and 1-Hexanol, both polar solutes, much better, while benzene can dissolve Cl_2 and cyclohexane, which are nonpolar, to a greater extent. The aptitude that each solvent has in dissolving the solutes directly correlate to the concentrations of solutes that are present in the solvent.

Thus, Jim would drink the ethanol, since it has the highest concentration of the polar 1-Hexanol. Also, the benzene would have the highest concentration of Cl_2 and cyclohexane, and the ethanol would also have the highest concentration of $CaCl_2$, which is ionic and therefore “very polar”.

Abstract: “Like dissolves Like”: polar solvents dissolve polar solutes, and nonpolar solvents dissolve polar solutes

Q106

Calculate the pH of a 0.5 M H_3PO_4 acid solution given that $K_{a1} = 7.1 \times 10^{-3}$, $K_{a2} = 6.3 \times 10^{-8}$ and $K_{a3} = 4.2 \times 10^{-13}$.

Solution

A14.106V2

1.25

H14.106V2

Review on how to calculate the pH of a polyprotic acids here.

S14.106V2

$$7.1 \times 10^{-3} = \frac{x^2}{(0.5 - x)}$$

$$x = 0.0561\ M = [H^+]$$

$$pH = -\log[H^+] = 1.25$$

We assume that all of the H^+ in solution comes from the dissociation of the first H^+ because the second and the third is too small to have a significant effect in the pH of the solution.

Q107

The Haber-Bosch process is a method invented in the 20th century as a method for hydrogen fixation. It is widely used in industry today, and involves reacting nitrogen and hydrogen in the following manner:

$$\mathrm{N_2\,(g) + 3\,H_2\,(g)\ \rightleftharpoons\ 2\,NH_3\,(g)}$$

Calculate ΔG°_{rxn}. If the pressure of the products and reaction are all kept constant at the same value, in which direction will the reaction go?

Relevant information:

$\Delta G^\circ_f\ \ NH_{2\,(g)} = 199.83 \frac{kJ}{mol}$

Solution

The process of calculating ΔG should be very familiar after reading Q15, so this solution will not elaborate much on this

method. With that being said, the ΔG°_{rxn} is as follows:

$$\Delta G^{\circ}_{rxn} = 399.66 \frac{kJ}{mol}$$

Both N_2 and H_2 have respective ΔG_f of zero. Now, remember that if ΔG°_{rxn} is negative (ΔG°_{rxn}<0), then the reaction is spontaneous in the direction mentioned. However, in this case the ΔG°_{rxn} is definitely NOT less than zero, so it is not spontaneous in the direction $N_{2\,(g)} + 3H_{2\,(g)} \rightarrow 2NH_{3\,(g)}$. However, if the chemical formula is "flipped" so that it goes from $N_{2\,(g)} + 3H_{2\,(g)} \leftarrow 2NH_{3\,(g)}$, Hess's law states that the corresponding ΔG°_{rxn} is also "flipped" from positive to negative (or vice versa, depending on the value. For this situation, however, the ΔG°_{rxn} does turn negative). What information can be drawn from this is that, since a negative ΔG°_{rxn} means that the reaction will be spontaneous, then it can be inferred that the reaction will favor going from $N_{2\,(g)} + 3H_{2\,(g)} \leftarrow 2NH_{3\,(g)}$, rather than $N_{2\,(g)} + 3H_{2\,(g)} \rightarrow 2NH_{3\,(g)}$. Without even having to calculate the equilibrium constant, from this information alone, it can be inferred that, at equilibrium, the reactants are favored over the products. Therefore, if both gasses are kept at constant pressure, the reaction will tend to increase concentration of reactants. Thus, the reaction will go left.

Abstract: Find the ΔG°_{rxn}, understand what implications it has in regards to equilibrium, and apply this knowledge to infer that the reaction will favor the reactants.

Q109

At 273 K, the equation: $H_2(g) + I_2(g) \rightarrow 2HI(g)$ has an equilibrium constant of 60.2

a. Solve for ΔG° at 273 K
b. How does G change when the pressure of HI is 2 atm, I_2 is 4 atm and H_2 is 6 atm?
c. Is this reaction spontaneous?

Solution

a) ΔG° = -RT ln(K)

ΔG° = -(8.3145 J/K mol)(273 K) ln(60.2)

ΔG° = -9301.1 J/mol

b) ΔG = ΔG° + RT ln(Q)

ΔG = -9301.1 J/mol + (8.3145 J/K mol)(273 K) ln(P_{HI} / $P_{H2}P_{I2}$)

ΔG = -9301.1 J/mol + (8.3145 J/K mol)(273 K) ln(2 / (6x4))

ΔG = -14941.49 J/mol.

c) This reaction proceeds spontaneously in the forward direction.

Q109

At 773 K the equilibrium constant for the Haber-Bosch process is 1.45×10^{-5}. The chemical reaction involved in the Haber-Bosch process is:

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

a. What is $\Delta G\,^{\circ}(773)$ for this reaction?
b. What is ΔG at 773 K for transforming 1 mole of N_2 and 3 moles H_2 held at 30 atm to 2 moles of NH_3 held at 1 atm?
c. In which direction would the previous reaction run spontaneously?

Solution

a. The value of $\Delta G\,°(773)$ can be found using the equation $\Delta G\,° = -RT\ln K$ where T and K are already known to be 773 K and 1.45x10^{-5} respectively while R=8.134 J K^{-1} mol^{-1}.

$$\Delta G°= -8.314\ J\ K^{-1}\ mol^{-1} \times 773K \times ln(1.45 \times 10^{-5}) = 70052\ J$$

$$\Delta G°= 70052\ J$$

b. The equation needed to determine ΔG is $\Delta G = RTln(Q/K)$. The values of R, T, and K are known while Q is

$$Q = \frac{P^2_{NH_3}/P_{ref}}{(P_{N_2}/P_{ref})(P^3_{H_2}/P_{ref})}$$

P_{ref} =1 atm and the other pressures are stated in the question. So to find Q, the pressures have to be plugged into the equation

$$Q = \frac{(1)^2}{(20)(20)^3} = \frac{1}{160000} = 6.25 \times 10^{-6}$$

Now that the value of Q is known, ΔG can be found

$$\Delta G = -8.314\ J\ K^{-1}\ mol^{-1} \times 773K \times ln(\frac{6.25 \times 10^{-6}}{1.45 \times 10^{-5}}) = -5291\ J$$

$$\Delta G = -5291\ J$$

c. The previous reaction would run towards the products spontaneously because $\Delta G < 0$.

Q111

The following reaction is exothermic

$$\mathrm{SnO_2\,(s) + 2\,H_2\,(g) \longrightarrow Sn\,(g) + 2\,H_2O\,(l)}$$

a. What is the equilibrium expression based on this chemical equation?
b. What happens to the reaction if more H_2 is added? SnO_2 is added into the system?
c. What effect would an increase in temperature have on the system?
d. What affect would an increase in pressure have on the system?

Solution

a. Add texts here. Do not delete this text first.K = [Sn] / [H_2] This is because solids are not included in the equilibrium expression
b. If H_2 were added, the reaction would shift right, towards the products, more Sn is produced. If SnO_2 were added, there would be no effect on the equilibrium because SnO_2 is not involve in the equilibrium process (K).
c. The reaction would shift towards the reactants. The reaction is exothermic, so heat is treated like a product.
d. An increase in pressure would shift the reaction towards the side that has less mole of gas. Therefore, in this reaction, an increased in pressure would shift the reaction to the right, more products are produced. Q111

Q112

Given the chemical reaction

$$\mathrm{SnO_2\,(s)\ \rightleftharpoons Sn\,(s) + O_2\,(g)}$$

a. Formulate the equilibrium expression using activities
b. State the effect on pO_2 at equilibrium if more $\mathrm{SnCl_4\,(l)}$ is added to the system
c. State the effect on pO_2 at equilibrium if more $\mathrm{O_2\,(g)}$ is added to the system

Solution

a. The activities of solids and liquids are always equal to 1. The activities of gases are equal to the partial pressure of the gas in bars. Therefore the equilibrium expression would be

$$K = P_{O_2}$$

b. P_{O_2} would not change because the activity of a liquid is always 1 meaning it has no effect on the equilibrium constant

c. P_{O_2} would decrease because the extra gas would push the system out of equilibrium and in order for the system to return to equilibrium, some of the O_2 gas would have to react with some of the $Sn_{(s)}$. This would decrease the amount of $O_{2(g)}$ present in the system and therefore decrease the the pressure of $O_{2(g)}$.

Q113

Arrange the following solutions in order of most acidic to basic: NaOH, NaCN, H_2SO_4, NH_4NO_3, NaCl

Solution

$$\mathrm{H_2SO_4 > NH_4NO_3 > NaCl > NaCN > NaOH} \tag{5.E.1617}$$

Review acids bases here.

- H_2SO_4 is a strong acid.
- NH_4NO_3 is formed by a weak base (NH_4OH) and a strong acid (HNO_3). Hence, NH_4NO_3 is acidic.
- NaCl is formed by a strong base (NaOH) and a strong acid (HCl). Hence, it is a neutral salt.
- NaCN is formed by a strong base (NaOH) and a weak acid (HCN). Hence, NaCN is basic.
- NaOH is a strong base.

Q115

Given that the K_b values for $\mathrm{NH_3}$ and $\mathrm{NH_2NH_2}$ are 1.8×10^{-5} and 8.5×10^{-7}, respectively. Which is the stronger acid?

Solution

$$\mathrm{NH_2NH_2}$$

Calculate the K_a values first. Review on how to identify the strength of an acid from its K_a value here.

For NH_3,

$$K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

For NH_2NH_2,

$$K_a = \frac{(1.0 \times 10^{-14}}{8.5 \times 10^{-7}} = 1.18 \times 10^{-8}$$

Since the Ka value of NH_2NH_2 is larger, NH_2NH_2 is the stronger acid.

Q119

Calculate the pH of the following solutions.

a. 0.5 M NaCN (K_a of $\mathrm{HCN} = 6.2 \times 10^{-10}$)
b. 0.01 M $\mathrm{NH_4Cl}$ (K_b of $\mathrm{NH_3} = 1.8 \times 10^{-5}$)

Solution

11.5 5.63

Ka=(1*10^{-14})/(1.8*10^{-5})=5.56*10^{-10}
5.56*10^{-10}=x^2/(0.01-x)
x=2.36*10^{-6}
pH= -log(x)= 5.63

H14.119V2

Review on the properties of salts here.

\[\ce{CN$^-$ (aq) + H$_2$O (l) <=> HCN (aq) + OH$^-$ (aq)}\]

Kb=(1*10^{-14})/(6.2*10^{-10})=1.62*10^{-5}

$$1.62 \times 10^{-5} = \frac{x^2}{0.5 - x} \tag{5.E.1618}$$

x=0.00283

pOH= -log(x)= 2.55

pH= 14-pOH= 11.5

$$\mathrm{NH_4{}^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)} \tag{5.E.1619}$$

Q131

Identify the stronger acid in each of the following combination. Explain.

a. HF and HBr
b. H_2SO_4 and H_2SO_3
c. HOCl and HOBr

Solution

14.131V2

HBr H_2SO_4 HOCl

Study the effect of structure on acids and bases.

S14.131V2

1. HBr is the stronger acid because Br less electronegative and therefore less polar as compared to HF.
2. H_2SO_4 is the stronger acid because as the number of attached oxygen on the O-H bonds increases, the less polar the molecule is.
3. For oxyacids, the less polar oxyacids are the ones that are more electronegative. Since Cl is more electronegative than Br, HOCl is the stronger acid.

Q137

Identify the Lewis acid and Lewis base for each of the following reaction.

a. $\mathrm{H^+(aq) + NH_3(aq) \rightleftharpoons NH_4{}^+(aq)}$

b. $Al^{3+}(aq) + 6\,H_2O(l) \rightleftharpoons Al(H_2O)_6{}^{3+}(aq)$
c. $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

Solution

	Lewis acid	Lewis base
1.	H^+	NH_3
2.	Al^{3+}	H_2O
3.	CO_2	H_2O

H14.137V2

Study the concept of electron pairs here.

S14.137V2

H^+ is the electron-pair acceptor while NH_3 is the electron-pair donor. Al^{3+} is the electron-pair acceptor while H_2O is the electron-pair donor. CO_2 is the electron-pair acceptor while H_2O is the electron-pair donor.

Q139

Beryllium hydroxide is an amphoteric compound. It can react as an acid as well as a base. Please write the reactions of $Be(OH)_2$ and describe its role base on Brønsted-Lowry and Lewis theories.

Solution

$Be(OH)_2(s)+2H^+(aq)$-> $Be^{2+}(aq)+2H_2O(l)$ (Brønsted-Lowry base, $2H^+$ acceptor)

$Be(OH)_2(s)+2OH^-(aq)$-> $Be(OH)_4{}^{2-}(aq)$ (Lewis acid, electron pair acceptor)

H14.139.2P

Consider Brønsted-Lowry and Lewis theories.

http://chemwiki.ucdavis.edu/Textbook...cids_and_Bases

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6.1: Classifications of Acids and Bases

Learning Objectives

- To understand the differences between the three definitions of Acids and Bases
- Identify acids, bases, and conjugate acid-base pairs according to the three definitions of Acids and Bases
- To understand the concept of conjugate acid–base pairs in acid/base reactions
- Write the equation for the proton transfer reaction involving a Brønsted-Lowry acid or base, and show how it can be interpreted as an **electron-pair transfer** reaction, clearly identifying the donor and acceptor.
- Give an example of a **Lewis acid-base reaction** that does not involve protons.

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Carl Axel Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Acids and bases are common solutions that exist everywhere. Almost every liquid that we encounter in our daily lives consists of acidic and basic properties, with the exception of water. They have completely different properties and are able to neutralize to form H_2O, which will be discussed later in a subsection. Acids and bases can be defined by their physical and chemical observations (Table 6.1.1).

Table 6.1.1: General Properties of Acids and Bases

ACIDS	BASES
produce a piercing pain in a wound.	give a slippery feel.
taste sour.	taste bitter.
are colorless when placed in phenolphthalein (an indicator).	are pink when placed in phenolphthalein (an indicator).
are red on blue litmus paper (a pH indicator).	are blue on red litmus paper (a pH indicator).
have a pH<7.	have a pH>7.
produce hydrogen gas when reacted with metals.	
produce carbon dioxide when reacted with carbonates.	
Common examples: Lemons, oranges, vinegar, urine, sulfuric acid, hydrochloric acid	Common Examples: Soap, toothpaste, bleach, cleaning agents, limewater, ammonia water, sodium hydroxide.

Acids and bases in aqueous solutions will conduct electricity because they contain dissolved ions. Therefore, acids and bases are *electrolytes*. Strong acids and bases will be strong **electrolytes**. Weak acids and bases will be weak electrolytes. This affects the amount of conductivity.

In chemistry, acids and bases have been defined differently by **three sets of theories**: One is the Arrhenius definition defined above, which revolves around the idea that acids are substances that ionize (break off) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide (OH^-) ions in solution. The other two definitions are discussed in detail include

the **Brønsted-Lowry definition** the defines acids as substances that donate protons (H^+) whereas bases are substances that accept protons and the **Lewis theory** of acids and bases states that acids are electron pair acceptors while bases are electron pair donors.

Arrhenius Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. The Arrhenius definition of acid-base reactions is a development of the "hydrogen theory of acids". It was used to provide a modern definition of acids and bases, and followed from Arrhenius's work with Friedrich Wilhelm Ostwald in establishing the presence of ions in aqueous solution in 1884. This led to Arrhenius receiving the Nobel Prize in Chemistry in 1903.

An **Arrhenius acid** is a compound that increases the concentration of $\mathrm{H^+}$ ions that are present when added to water.

[redacted]

In this reaction, hydrochloric acid (HCl) gas dissociates into hydrogen ($\mathrm{H^+}$) and chloride ($\mathrm{Cl^-}$) ions when dissolved in water, thereby releasing $\mathrm{H^+}$ ions into solution. These $\mathrm{H^+}$ ions form the hydronium ion ($\mathrm{H_3O^+}$) when they combine with water molecules. Both processes can be represented in a chemical equation by adding $\mathrm{H_2O}$ to the reactants side of Equation 9.5.728 and switching hydronium ions for free protons.

[redacted]

An **Arrhenius base** is a compound that dissociates to yield hydroxide ions ($\mathrm{OH^-}$) in aqueous solution. Common examples of Arrhenus bases include Sodium hydroxide (NaOH), Potassium hydroxide (KOH), Magnesium hydroxide $\mathrm{Mg(OH)_2}$, and Calcium hydroxide ($\mathrm{Ca(OH)_2}$. All of these bases are solids at room temperature and when dissolved in water, will generate a metal cation and the hydroxide ion ([redacted]), for example, Sodium hydroxide

[redacted]

All Arrhenius acids have easily detachable hydrogen that leave to form hydronium ions in solution and all Arrhenius bases have easily detachable OH groups that form hydroxide ions in solution.

Limitation of the Arrhenius Definition of Acids and Bases

The Arrhenius definitions of acidity and alkalinity are restricted to aqueous solutions and refer to the concentration of the solvated ions. Under this definition, pure $\mathrm{H_2SO_4}$ or HCl dissolved in toluene are not acidic, despite the fact that both of these acids will donate a proton to toluene. In addition, under the Arrhenius definition, a solution of sodium amide ($\mathrm{NaNH_2}$) in liquid ammonia is not alkaline, despite the fact that the amide ion ($\mathrm{NH_2^-}$) will readily deprotonate ammonia. Thus, the Arrhenius definition can only describe acids and bases in an aqueous environment. The Arrhenius definition can **only** describe acids and bases in protic solvents and environments (e.g., water, alcohols, within proteins etc.).

Brønsted-Lowry Acids and Bases

The Arrhenius definitions identified an acid as a compound that dissolves in water to yield hydronium ions (Equation 6.1.1211 \) and a base as a compound that dissolves in water to yield hydroxide ions (Equation 6.1.1212). As mentioned above, this definition limited. We extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, $\mathrm{H^+}$. A proton is what remains when a normal hydrogen atom, $\mathrm{^1_1H}$, loses an electron. A compound that donates a proton to another compound is called a **Brønsted-Lowry acid**, and a compound that accepts a proton is called a **Brønsted-Lowry base**. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base).

Acids may be compounds such as HCl or $\mathrm{H_2SO_4}$, organic acids like acetic acid ($\mathrm{CH_3COOH}$) or ascorbic acid (vitamin C), or $\mathrm{H_2O}$. Anions (such as $\mathrm{HSO_4^-}$, $\mathrm{H_2PO_4^-}$, $\mathrm{HS^-}$, and $\mathrm{HCO_3^-}$) and cations (such as $\mathrm{H_3O^+}$, $\mathrm{NH_4^+}$, and $\mathrm{[Al(H_2O)_6]^{3+}}$) may also act as acids.

Bases fall into the same three categories and may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, $HCO_3{}^-$, $CO_3{}^{2-}$, F^-, and $PO_4{}^{3-}$), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as $NaOH$ and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

[redacted]

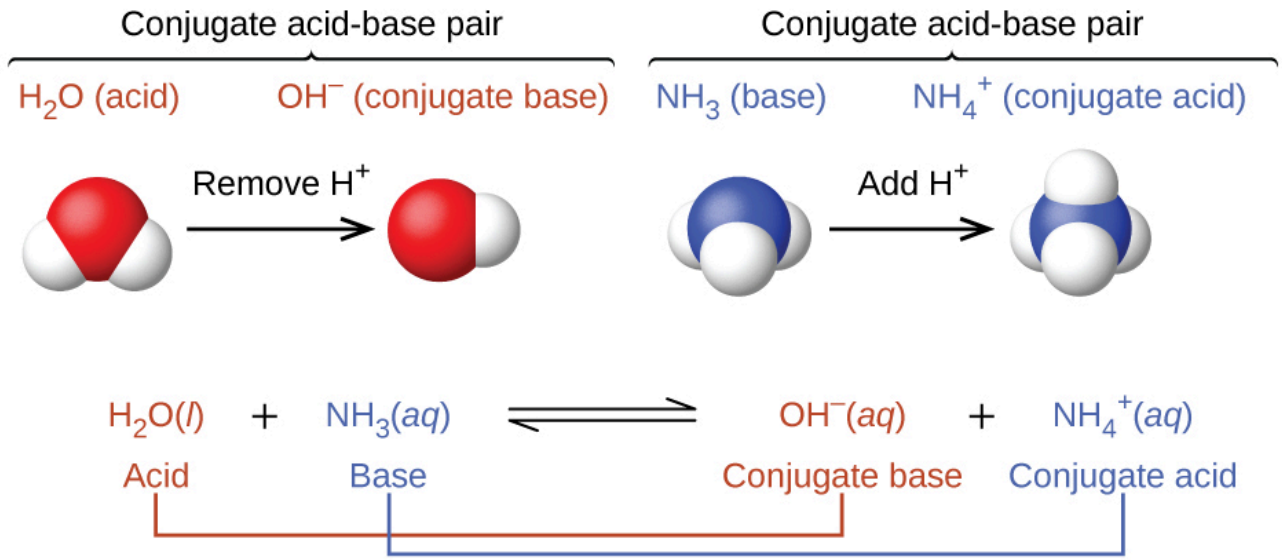
We call the product that remains after an acid donates a proton the **conjugate base** of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base}$$
$$HF \rightleftharpoons H^+ + F^-$$
$$H_2SO_4 \rightleftharpoons H^+ + HSO_4{}^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$
$$HSO_4{}^- \rightleftharpoons H^+ + SO_4{}^{2-}$$
$$NH_4{}^+ \rightleftharpoons H^+ + NH_3$$

We call the product that results when a base accepts a proton the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base):

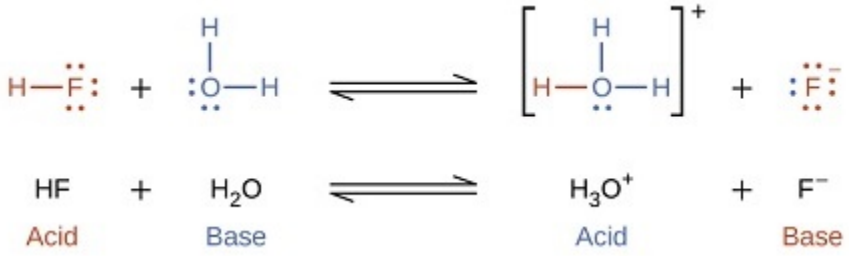
$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid}$$
$$OH^- + H^+ \rightleftharpoons H_2O$$
$$H_2O + H^+ \rightleftharpoons H_3O^+$$
$$NH_3 + H^+ \rightleftharpoons NH_4{}^+$$
$$S^{2-} + H^+ \rightleftharpoons HS^-$$
$$CO_3{}^{2-} + H^+ \rightleftharpoons HCO_3{}^-$$
$$F^- + H^+ \rightleftharpoons HF$$

In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, $NH_4{}^+$:



The reaction between a Brønsted-Lowry acid and water is called acid ionization. For example, when hydrogen fluoride dissolves

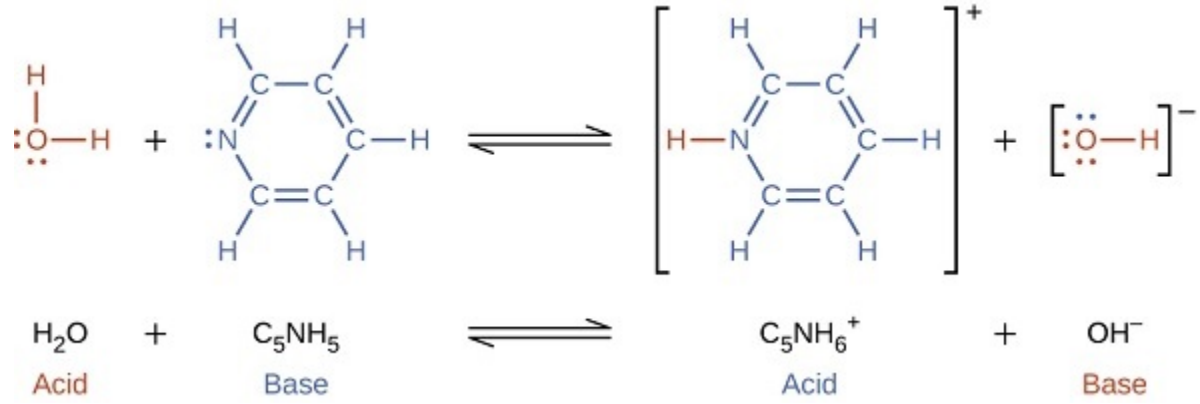
in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



with

$$K = \frac{[\mathrm{H_3O^+}][\mathrm{F^-}]}{[\mathrm{HF}]}$$

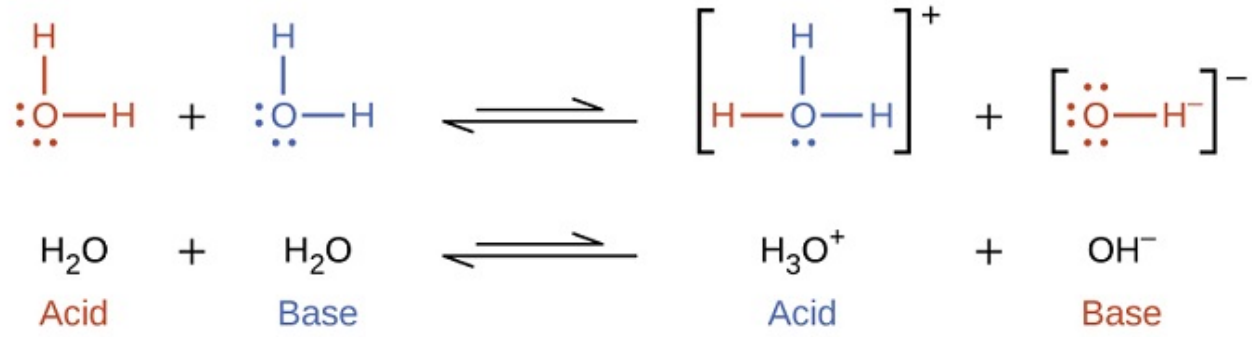
When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding ammonia to water yields hydroxide ions and ammonium ions:



with

$$K = \frac{[\mathrm{C_5NH_6^+}][\mathrm{OH^-}]}{[\mathrm{C_5NH_5}]}$$

Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$\mathrm{H_2O\,(l) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)} \tag{6.1.1620}$$

with

[redacted]

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is approximately 5.1×10^{-13}, roughly 100-times larger than the value at 25 °C.

Example 6.1.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[\mathrm{H_3O^+}] = [\mathrm{OH^-}]$. At 25 °C:

$$\begin{aligned} K_\mathrm{w} &= [\mathrm{H_3O^+}][\mathrm{OH^-}] \\ &= [\mathrm{H_3O^+}]^2 \\ &= [\mathrm{OH^-}]^2 \\ &= 1.0 \times 10^{-14} \end{aligned}$$

So

$$[\mathrm{H_3O^+}] = [\mathrm{OH^-}] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

Exercise 6.1.1

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$$[\mathrm{H_3O^+}] = [\mathrm{OH^-}] = 4.9 \times 10^{-7}\ M$$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. Example 6.1.2 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

Example 6.1.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

The Inverse Proportionality of [H_3O^+] and [OH^-] A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of [H_3O^+]:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Chatelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Exercise 6.1.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M$$

Amphoteric Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic. Another term used to describe such species is amphoteric, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons CO_3^{2-}\,(aq) + H_3O^+\,(aq)$$

$$HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) + OH^-\,(aq)$$

Example 6.1.3: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of $\mathrm{HSO_3}^-$

a. as an acid with OH^-
b. as a base with HI

Solution

a. $\mathrm{HSO_3}^-(aq) + \mathrm{OH}^-(aq) \rightleftharpoons \mathrm{SO_3}^{2-}(aq) + \mathrm{H_2O}_{(l)}$
b. $\mathrm{HSO_3}^-(aq) + \mathrm{HI}(aq) \rightleftharpoons \mathrm{H_2SO_3}(aq) + \mathrm{I}^-(aq)$

Exercise 6.1.3

Write separate equations representing the reaction of $\mathrm{H_2PO_4}^-$

a. as a base with HBr
b. as an acid with OH^-

Answer a

$$\mathrm{H_2PO_4}^-(aq) + \mathrm{HBr}(aq) \rightleftharpoons \mathrm{H_3PO_4}(aq) + \mathrm{Br}^-(aq)$$

Answer b

$$\mathrm{H_2PO_4}^-(aq) + \mathrm{OH}^-(aq) \rightleftharpoons \mathrm{HPO_4}^{2-}(aq) + \mathrm{H_2O}_{(l)}$$

Lewis Acids and Bases

The Brønsted-Lowry proton donor-acceptor concept has been one of the most successful theories of Chemistry. But as with any such theory, it is fair to ask if this is not just a special case of a more general theory that could encompass an even broader range of chemical science. In 1916, G.N. Lewis of the University of California proposed that the *electron pair* is the dominant actor in acid-base chemistry. The Lewis theory did not become very well known until about 1923 (the same year that Brønsted and Lowry published their work), but since then it has been recognized as a very powerful tool for describing chemical reactions of widely different kinds and is widely used in organic and inorganic chemistry. The Brønsted–Lowry concept of acids and bases defines a base as any species that can accept a proton, and an acid as any substance that can donate a proton. Lewis proposed an alternative definition that focuses on *pairs of electrons* instead. According to Lewis:

- An *acid* is a substance that **accepts** a pair of electrons, and in doing so, forms a covalent bond with the entity that supplies the electrons.
- A *base* is a substance that **donates** an unshared pair of electrons to a recipient species with which the electrons can be shared.

In modern chemistry, electron donors are often referred to as nucleophiles, while acceptors are electrophiles.

Lewis Acid-Base Neutralization Involving Electron-Pair Transfer

Just as any Arrhenius acid is also a Brønsted acid, any Brønsted acid is also a Lewis acid, so the various acid-base concepts are all "upward compatible". Although we do not really need to think about electron-pair transfers when we deal with ordinary aqueous-solution acid-base reactions, it is important to understand that it is the opportunity for electron-pair sharing that enables proton transfer to take place.



This equation for a simple acid-base neutralization shows how the Brønsted and Lewis definitions are really just different views of the same process. Take special note of the following points:

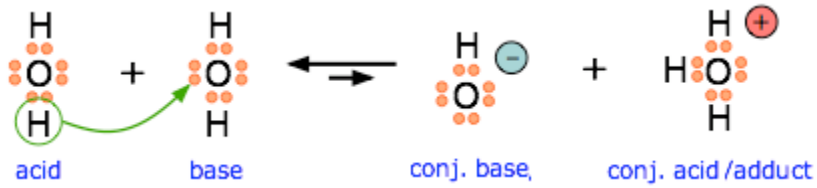
- The arrow shows the movement of a proton from the hydronium ion to the hydroxide ion.
- Note that the electron-pairs themselves do not move; they remain attached to their central atoms. The electron pair on the base is "donated" to the acceptor (the proton) only in the sense that it ends up being *shared* with the acceptor, rather than being the exclusive property of the oxygen atom in the hydroxide ion.
- Although the hydronium ion is the nominal Lewis acid here, it does not itself accept an electron pair, but acts merely as the source of the proton that coordinates with the Lewis base.

Note

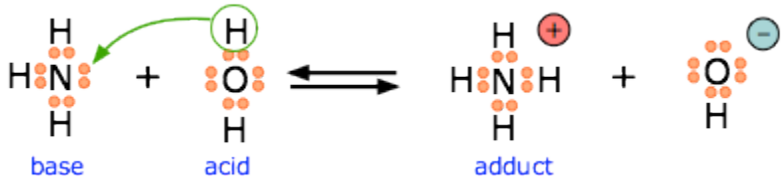
The point about the electron-pair remaining on the donor species is especially important to bear in mind. For one thing, it distinguishes a *Lewis acid-base reaction* from an *oxidation-reduction reaction*, in which a physical transfer of one or more electrons from donor to acceptor does occur.

The product of a Lewis acid-base reaction is known formally as an "**adduct**" or "complex", although we do not ordinarily use these terms for simple proton-transfer reactions such as the one in the above example. Here, the proton combines with the hydroxide ion to form the "adduct" $\mathrm{H_2O}$. The following examples illustrate these points for some other proton-transfer reactions that you should already be familiar with.

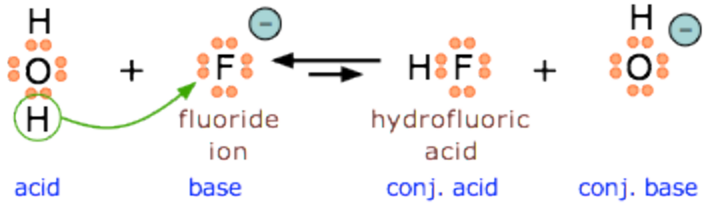
Another example, showing the autoprotolysis of water. Note that the conjugate acid is also the adduct.



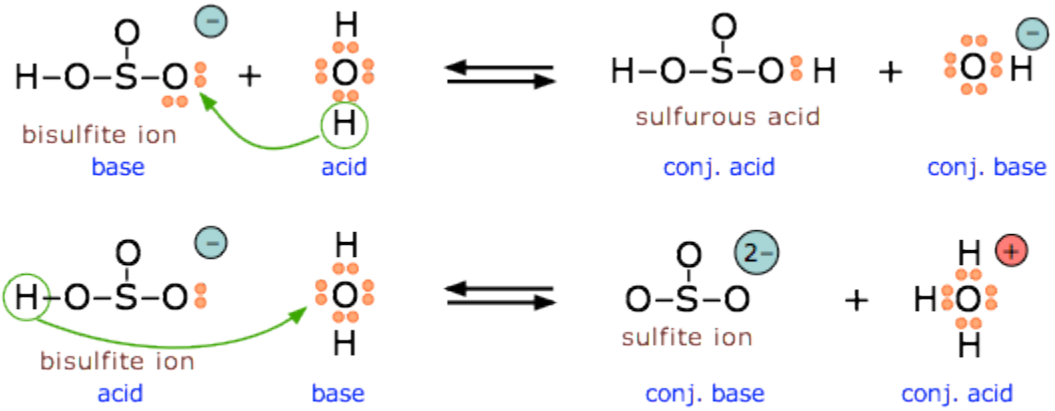
Ammonia is both a Brønsted and a Lewis base, owing to the unshared electron pair on the nitrogen. The reverse of this reaction represents the *hydrolysis* of the ammonium ion.



Because HF is a weak acid, fluoride salts behave as bases in aqueous solution. As a Lewis base, $\mathrm{F^-}$ accepts a proton from water, which is transformed into a hydroxide ion.



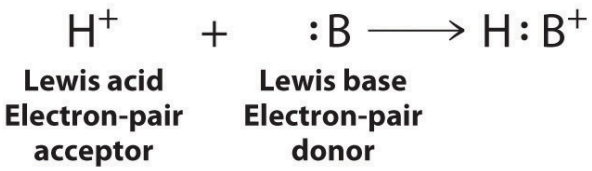
The bisulfite ion is *amphiprotic* and can act as an electron donor or acceptor.



All Brønsted–Lowry bases (proton acceptors), such as $\mathrm{OH^-}$, $\mathrm{H_2O}$, and $\mathrm{NH_3}$, are also electron-pair donors. Thus the Lewis definition of acids and bases does not contradict the Brønsted–Lowry definition. Rather, it expands the definition of acids to include substances other than the $\mathrm{H^+}$ ion.

Lewis Acid-Base Neutralization without Transferring Protons

Electron-deficient molecules, such as BCl_3, contain less than an octet of electrons around one atom and have a strong tendency to gain an additional pair of electrons by reacting with substances that possess a lone pair of electrons. Lewis's definition, which is less restrictive than either the Brønsted–Lowry or the Arrhenius definition, grew out of his observation of this tendency. A general Brønsted–Lowry acid–base reaction can be depicted in Lewis electron symbols as follows:

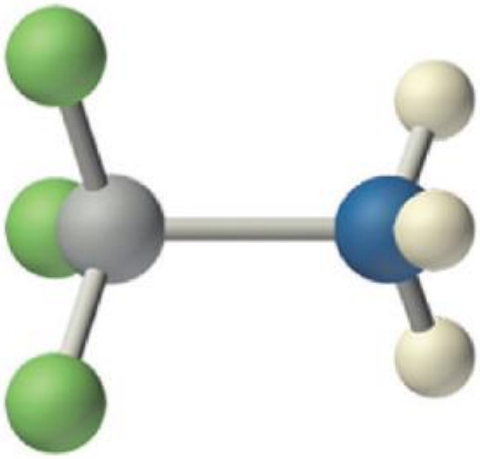


The proton (H^+), which has no valence electrons, is a Lewis acid because it accepts a lone pair of electrons on the base to form a bond. The proton, however, is just one of many electron-deficient species that are known to react with bases. For example, neutral compounds of boron, aluminum, and the other Group 13 elements, which possess only six valence electrons, have a very strong tendency to gain an additional electron pair. Such compounds are therefore potent Lewis acids that react with an electron-pair donor such as ammonia to form an acid–base adduct, a new covalent bond, as shown here for boron trifluoride (BF_3):

$$BF_3 + :NH_3 \longrightarrow F_3B:NH_3$$

Lewis acid **Lewis base** **Acid-base adduct**

The bond formed between a Lewis acid and a Lewis base is a **coordinate covalent bond** because both electrons are provided by only one of the atoms (N, in the case of $F_3B:NH_3$). After it is formed, however, a coordinate covalent bond behaves like any other covalent single bond.



Boron trifluoride-ammonia adduct

Species that are very weak Brønsted–Lowry bases can be relatively strong Lewis bases. For example, many of the group 13 trihalides are highly soluble in ethers (R–O–R′) because the oxygen atom in the ether contains two lone pairs of electrons, just as in H_2O. Hence the predominant species in solutions of electron-deficient trihalides in ether solvents is a Lewis acid–base adduct. A reaction of this type is shown in Figure 6.1.1 for boron trichloride and diethyl ether:

$$BCl_3 + :\ddot{O}(CH_2CH_3)_2 \longrightarrow Cl_3B:\ddot{O}(CH_2CH_3)_2$$

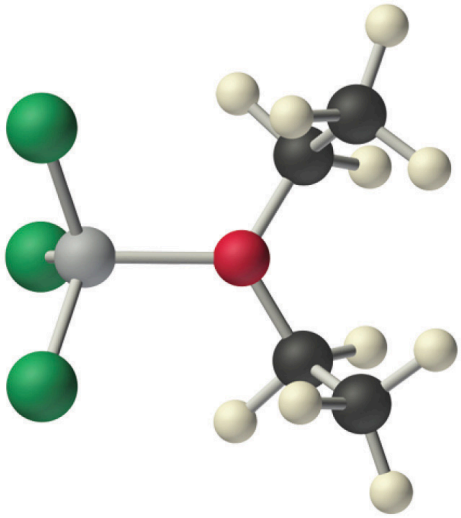
Lewis acid **Lewis base** **Acid-base adduct**

Figure 6.1.1: Lewis Acid/Base reaction of boron trichloride and diethyl ether reaction

Note

- Electron-deficient molecules (those with less than an octet of electrons) are Lewis acids.
- The acid-base behavior of many compounds can be explained by their Lewis electron structures.

Many molecules with multiple bonds can act as Lewis acids. In these cases, the Lewis base typically donates a pair of electrons to form a bond to the central atom of the molecule, while a pair of electrons displaced from the multiple bond becomes a lone pair on a terminal atom.



Boron trichloride-diethyl ether adduct

Figure 6.1.2: The highly electronegative oxygen atoms pull electron density away from carbon, so the carbon atom acts as a Lewis acid. Arrows indicate the direction of electron flow.

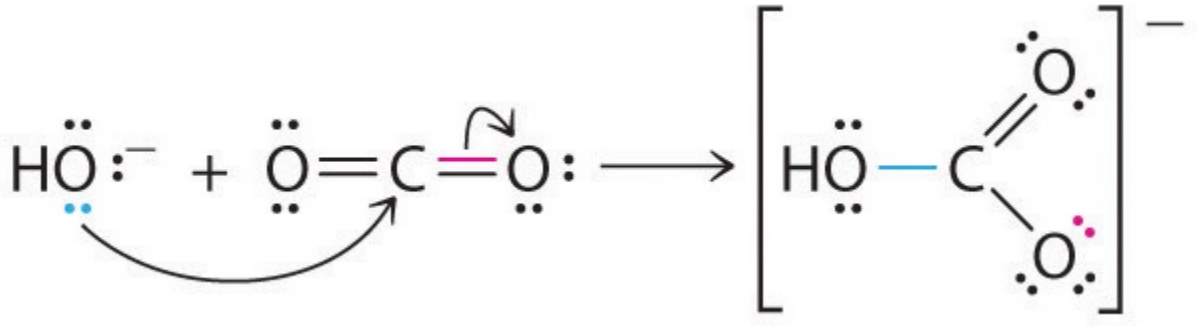


Figure 6.1.2: Lewis Acid/Base reaction of the hydroxide ion with carbon dioxide

Example 6.1.4

Identify the acid and the base in each Lewis acid–base reaction.

a. $BH_3 + (CH_3)_2S \rightarrow H_3B{:}S(CH_3)_2$
b. $CaO + CO_2 \rightarrow CaCO_3$
c. $BeCl_2 + 2\ Cl^- \rightarrow BeCl_4^{2-}$

Given: reactants and products

Asked for: identity of Lewis acid and Lewis base

Strategy:

In each equation, identify the reactant that is electron deficient and the reactant that is an electron-pair donor. The electron-deficient compound is the Lewis acid, whereas the other is the Lewis base.

Solution:

a. In BH_3, boron has only six valence electrons. It is therefore electron deficient and can accept a lone pair. Like oxygen, the sulfur atom in $(CH_3)_2S$ has two lone pairs. Thus $(CH_3)_2S$ donates an electron pair on sulfur to the boron atom of BH_3. The Lewis base is $(CH_3)_2S$, and the Lewis acid is BH_3.
b. As in the reaction shown in Equation 8.21, CO_2 accepts a pair of electrons from the O^{2-} ion in CaO to form the carbonate ion. The oxygen in CaO is an electron-pair donor, so CaO is the Lewis base. Carbon accepts a pair of electrons, so CO_2 is the Lewis acid.
c. The chloride ion contains four lone pairs. In this reaction, each chloride ion donates one lone pair to $BeCl_2$, which has only four electrons around Be. Thus the chloride ions are Lewis bases, and $BeCl_2$ is the Lewis acid.

Exercise 6.1.4A

Identify the acid and the base in each Lewis acid–base reaction.

a. $(CH_3)_2O + BF_3 \rightarrow (CH_3)_2O{:}BF_3$
b. $H_2O + SO_3 \rightarrow H_2SO_4$

Answer a

Lewis base: $(CH_3)_2O$; Lewis acid: BF_3

Answer b

Lewis base: H_2O; Lewis acid: SO_3

Exercise 6.1.4B

Here are several more examples of Lewis acid-base reactions that **cannot** be accommodated within the Brønsted or Arrhenius models. Identify the Lewis acid and Lewis base in each reaction.

a. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$
b. $SnS_2 + S^{2-} \rightarrow SnS_3^{2-}$
c. $Cd(CN)_2 + 2CN^- \rightarrow Cd(CN)_4^{2+}$
d. $AgCl + 2NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$
e. $Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$
f. $[Ni^{2+} + 6NH_3 \rightarrow Ni(NH_3)_5^{2+}$

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Video 6.1.1: Overview of Lewis Acids and Bases

Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°C$$

Glossary

acid ionization
: reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic
: species that may either gain or lose a proton in a reaction

amphoteric
: species that can act as either an acid or a base

autoionization
: reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization
reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid
proton donor

Brønsted-Lowry base
proton acceptor

conjugate acid
substance formed when a base gains a proton

conjugate base
substance formed when an acid loses a proton

ion-product constant for water (K_w)
equilibrium constant for the autoionization of water

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6.2: The Brønsted-Lowry Scheme

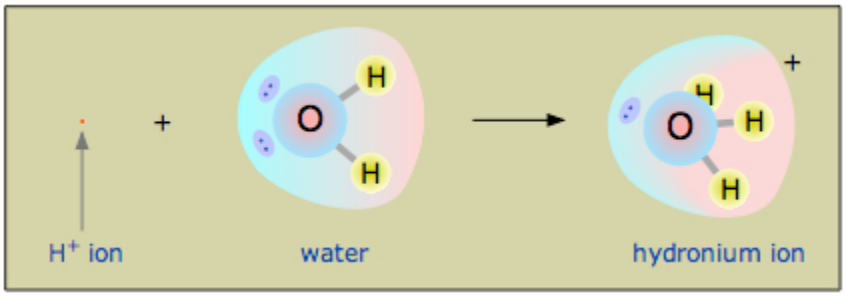
Learning Objectives

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- To know the relationship between acid or base strength and the magnitude of K_a, K_b, pK_a, and pK_b.
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

We now turn our attention to acid–base reactions to see how the concepts of chemical equilibrium and equilibrium constants can deepen our understanding of this kind of chemical behavior. We begin with a qualitative description of acid–base equilibria in terms of the Brønsted–Lowry model and then proceed to a quantitative description the following sections.

Free Hydrogen Ions do not Exist in Water

Owing to the overwhelming excess of H_2O molecules in aqueous solutions, a bare hydrogen ion has no chance of surviving in water. The hydrogen ion in aqueous solution is no more than a proton, a bare nucleus. Although it carries only a single unit of positive charge, this charge is concentrated into a volume of space that is only about a hundred-millionth as large as the volume occupied by the smallest atom. (Think of a pebble sitting in the middle of a sports stadium!) The resulting extraordinarily high *charge density* of the proton strongly attracts it to any part of a nearby atom or molecule in which there is an excess of negative charge. In the case of water, this will be the lone pair (unshared) electrons of the oxygen atom; the tiny proton will be buried within the lone pair and will form a shared-electron (coordinate) bond with it, creating a *hydronium ion*, H_3O^+. In a sense, H_2O is acting as a base here, and the product H_3O^+ is the conjugate acid of water:



Although other kinds of dissolved ions have water molecules bound to them more or less tightly, the interaction between H^+ and H_2O is so strong that writing "$H^+(aq)$" hardly does it justice, although it is formally correct. The formula H_3O^+ more adequately conveys the sense that it is both a molecule in its own right, and is also the conjugate acid of water. However, the equation

$$HA \longrightarrow H^+ + A^-$$

is so much easier to write that chemists still use it to represent acid-base reactions in contexts in which the proton donor-acceptor mechanism does not need to be emphasized. Thus it is permissible to talk about "hydrogen ions" and use the formula H^+ in writing chemical equations as long as you remember that they are not to be taken literally in the context of aqueous solutions.

Interestingly, experiments indicate that the proton does not stick to a single H_2O molecule, but changes partners many times per second. This molecular promiscuity, a consequence of the uniquely small size and mass the proton, allows it to move through the solution by rapidly hopping from one H_2O molecule to the next, creating a new H_3O^+ ion as it goes. The overall effect is the same as if the H_3O^+ ion itself were moving. Similarly, a hydroxide ion, which can be considered to be a "proton hole" in the water, serves as a landing point for a proton from another H_2O molecule, so that the OH^- ion hops about in the same way.

The **hydronium** ion is an important factor when dealing with chemical reactions that occur in aqueous solutions. Because hydronium and hydroxide ions can "move without actually moving" and thus without having to plow their way through the solution

by shoving aside water molecules as do other ions, solutions which are acidic or alkaline have extraordinarily high *electrical conductivities*. The hydronium ion has a trigonal pyramidal geometry and is composed of three hydrogen atoms and one oxygen atom. There is a lone pair of electrons on the oxygen giving it this shape. The bond angle between the atoms is 113 degrees.

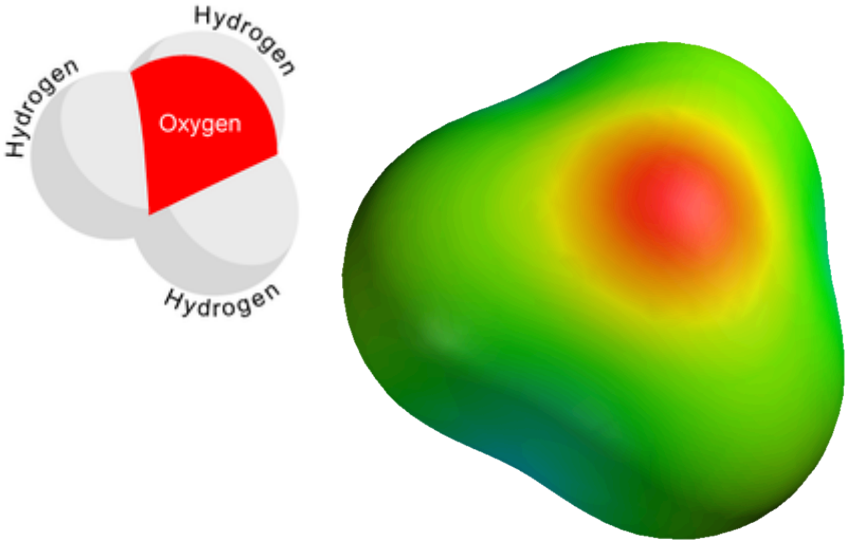


Figure 6.2.1. The picture above illustrates the electron density of hydronium. The red area represents oxygen; this is the area where the electrostatic potential is the highest and the electrons are most dense.

As H^+ ions are formed, they bond with H_2O molecules in the solution to form H_3O^+ (the hydronium ion). This is because hydrogen ions do not exist in aqueous solutions, but take the form the hydronium ion, H_3O^+. A reversible reaction is one in which the reaction goes both ways. In other words, the water molecules dissociate while the OH^- ions combine with the H^+ ions to form water. Water has the ability to attract H^+ ions because it is a polar molecule. This means that it has a partial charge, in this case the charge is negative. The partial charge is caused by the fact that oxygen is more electronegative than hydrogen. This means that in the bond between hydrogen and oxygen, oxygen "pulls" harder on the shared electrons thus causing a partial negative charge on the molecule and causing it to be attracted to the positive charge of H^+ to form **hydronium**. Another way to describe why the water molecule is considered polar is through the concept of dipole moment. The electron geometry of water is tetrahedral and the molecular geometry is bent. This bent geometry is asymmetrical, which causes the molecule to be polar and have a dipole moment, resulting in a partial charge.

The pH Scale

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is neutral if it contains equal concentrations of hydronium and hydroxide ions; acidic if it contains a greater concentration of hydronium ions than hydroxide ions; and basic if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities, the values of which may span many orders of magnitude, is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

[redacted]

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

[redacted]

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

or

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$\begin{aligned} K_{\mathrm{w}} &= [\mathrm{H_3O^+}][\mathrm{OH^-}] \\ -\log K_{\mathrm{w}} &= -\log([H_3O^+][OH^-]) \\ &= -\log[H_3O^+] + -\log[OH^-] \\ pK_w &= pH + pOH \end{aligned}$$

At 25 °C, the value of K_w is 1.0×10^{-14} and so:

The hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7}\ M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities less than $1.0 \times 10^{-7}\ M$ (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7}\ M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} *M*, which corresponds to pH and pOH values of:

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table 6.2.1).

Table 6.2.1: Summary of Relations for Acidic, Basic and Neutral Solutions

Classification	Relative Ion Concentrations	pH at 25 °C	pH at 80 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7	pH < 6.31
neutral	$[H_3O^+] = [OH^-]$	pH = 7	pH = 6.31
basic	$[H_3O^+] < [OH^-]$	pH > 7	pH > 6.31

Figure 6.2.2 shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH, and gives values for these properties at standard temperatures for some common substances.

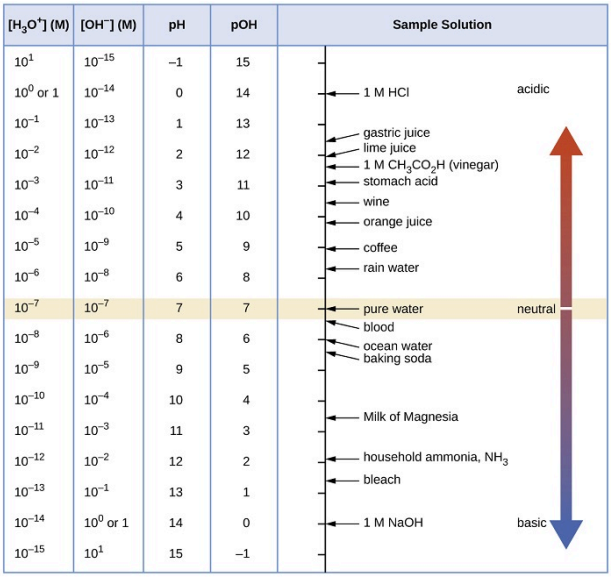


Figure 6.2.2: The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

Example 6.2.1: Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$?

Solution

$$\begin{aligned} \text{pH} &= -\log[H_3O^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) = 2.92 \end{aligned}$$

Exercise 6.2.1

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$\mathrm{CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}}$$

Air-saturated water has a hydronium ion concentration caused by the dissolved CO_2 of $2.0 \times 10^{-6}\ M$, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer

5.70

Example 6.2.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3.

Solution

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = 7.3$$
$$[\mathrm{H_3O^+}] = 10^{-7.3}$$
$$[\mathrm{H_3O^+}] = 5 \times 10^{-8}\ M$$

(On a calculator take the antilog, or the "inverse" log, of –7.3, or calculate $10^{-7.3}$.)

Exercise 6.2.2A

Calculate the hydronium ion concentration of a solution with a pH of –1.07.

Answer

12 M

This uses the definition of pH that we commonly use:

$$pH = -\log[H_3O^+]$$

So for this solution:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -1.07$$
$$[\mathrm{H_3O^+}] = 10^{+1.07}$$
$$= 12\,(\text{with significant figure})$$

However, at this high concentration, the solution will be non-ideal and we have to use the proper definition in terms of hydronium activities

$$pH = -\log a\{H_3O^+\}$$

See this module for more details.

Exercise 6.2.2B

The ionization constant of water K_w at 37 °C is 2.42×10^{-14}. What is the pH for a neutral solution at this human physiological temperature? Is the water acidic, basic or neutral?

Answer

$$\mathrm{K}_w = [\mathrm{H_3O^+}]\ [\mathrm{OH^-}] = 2.42 \times 10^{-14}$$

and

$$[\mathrm{H_3O^+}] = [\mathrm{OH^-}] = \sqrt{2.42 \times 10^{-14}}$$
$$= 1.55 \times 10^{-7}$$
$$pH = -\log[H_3O^+] = -\log 1.55 \times 10^{-7} = 6.81 \qquad (6.2.1621)$$

If we use the definition of acidic systems like in Figure 6.2.2, then we would (incorrectly) argue the solution is acidic. However, since $[\mathrm{OH^-}] = [\mathrm{H_3O^+}]$, the solution is still neutral. This is only a strange idea, if one ignores the temperature dependence of K_w.

Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

[redacted]

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

[redacted]

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.



Figure 6.2.3: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 6.2.3). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure 6.2.4).

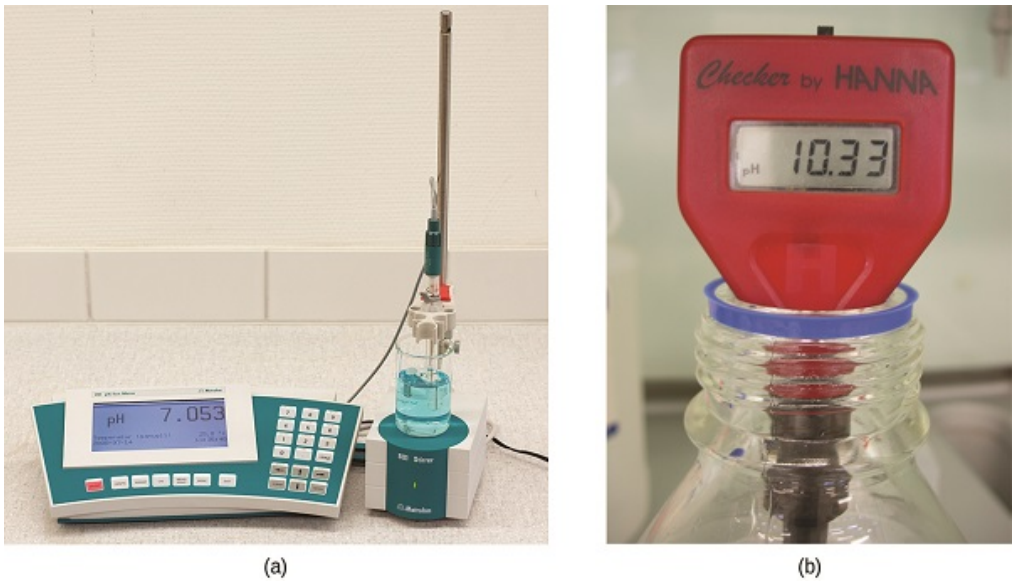


Figure 6.2.4: (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther).

Example 6.2.3: Calculation of pOH

What are the pOH and the pH of a 0.0125-M solution of potassium hydroxide, KOH at 25 °C?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[OH^-]$ = 0.0125 M:

$$\mathrm{pOH} = -\log[\mathrm{OH}^-] = -\log 0.0125 \tag{6.2.1622}$$

$$= -(-1.903) = 1.903 \tag{6.2.1623}$$

The pH can be found from the pOH:

$$\mathrm{pH} + \mathrm{pOH} = 14.00 \tag{6.2.1624}$$

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 1.903 = 12.10 \tag{6.2.1625}$$

Exercise 6.2.3

The hydronium ion concentration of vinegar is approximately $4 \times 10^{-3}\ M$ at 25 °C. What are the corresponding values of pOH and pH?

Answer

pOH = 11.6, pH = 2.4

The pH of a solution may also be visually estimated using colored indicators (Figure 6.2.5).



(a) (b)

Figure 6.2.5: (a) A universal indicator assumes a different color in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-M solutions of progressively weaker acids: HCl (pH = l), CH_3CO_2H (pH = 3), and NH_4Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-M solutions of the progressively stronger bases: KCl (pH = 7), aniline, $C_6H_5NH_2$ (pH = 9), NH_3 (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa).

Summary

The concentration of hydronium ion in a solution of an acid in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of hydroxide ion in a solution of a base in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of H_3O^+ in a solution can be expressed as the pH of the solution; $\mathrm{pH} = -\log \mathrm{H_3O^+}$. The concentration of OH^- can be expressed as the pOH of the solution: $\mathrm{pOH} = -\log[\mathrm{OH^-}]$. In pure water, pH = 7.00 and pOH = 7.00

Key Equations

- $\mathrm{pH} = -\log[\mathrm{H_3O^+}]$
- $\mathrm{pOH} = -\log[\mathrm{OH^-}]$
- $[H_3O^+] = 10^{-\mathrm{pH}}$
- $[OH^-] = 10^{-\mathrm{pOH}}$
- pH + pOH = pK_w = 14.00 at 25 °C

Glossary

acidic
: describes a solution in which $[H_3O^+] > [OH^-]$

basic
: describes a solution in which $[H_3O^+] < [OH^-]$

neutral
: describes a solution in which $[H_3O^+] = [OH^-]$

pH
: logarithmic measure of the concentration of hydronium ions in a solution

pOH
: logarithmic measure of the concentration of hydroxide ions in a solution

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6.3: Acid and Base Strength

Learning Objectives

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{6.3.1626}$$

Water is the base that reacts with the acid HA, $\mathrm{A^-}$ is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ when the acid ionizes in water; Figure $6.3.1$ lists several strong acids. A weak acid gives small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Figure $6.3.1$: Some of the common strong acids and bases are listed here.

Six Strong Acids		Six Strong Bases	
$\mathrm{HClO_4}$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\mathrm{Ca(OH)_2}$	calcium hydroxide
$\mathrm{HNO_3}$	nitric acid	$\mathrm{Sr(OH)_2}$	strontium hydroxide
$\mathrm{H_2SO_4}$	sulfuric acid	$\mathrm{Ba(OH)_2}$	barium hydroxide

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid HA:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{6.3.1627}$$

we write the equation for the ionization constant as:

$$K_\mathrm{a} = \frac{[H3O+][A-]}{[HA]} \tag{6.3.1628}$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is also the solvent. If the solution is assumed to be dilute, the activity of the water is approximated by the activity of pure water, which is defined as having a value of 1. The larger the K_a of an acid, the larger the concentration of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ relative to the concentration of the nonionized acid, HA. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase.

The following data on acid-ionization constants indicate the order of acid strength: $\mathrm{CH_3CO_2H} < \mathrm{HNO_2} < \mathrm{HSO_4^-}$

$$\begin{aligned} \mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2{}^-}(aq) \qquad K_\mathrm{a} = 1.8 \times 10^{-5} \\ \mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{NO_2{}^-}(aq) \qquad K_\mathrm{a} = 4.6 \times 10^{-4} \\ \mathrm{HSO_4{}^-}(aq) + \mathrm{H_2O}(aq) &\rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4{}^{2-}}(aq) \qquad K_\mathrm{a} = 1.2 \times 10^{-2} \end{aligned} \tag{6.3.1629}$$

Another measure of the strength of an acid is its *percent ionization*. The percent ionization of a weak acid is the ratio of the

concentration of the ionized acid to the initial acid concentration, times 100:

[redacted]

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

Example 6.3.1: Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[H3O+]_{eq}}{[HNO2]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NO_2}^-(aq) + \mathrm{H_3O}^+(aq).$$

Since $10^{-pH} = [\mathrm{H_3O}^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}\ M$, so that percent ionization (Equation 6.3.1237) is:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

Exercise 6.3.1

Calculate the percent ionization of a 0.10 *M* solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB}^+(aq) + \mathrm{OH}^-(aq) \tag{6.3.1630}$$

Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yields 100% (or very nearly so) of OH^- and HB^+ when it reacts with water; Figure 6.3.1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB}^+(aq) + \mathrm{OH}^-(aq), \tag{6.3.1631}$$

we write the equation for the ionization constant as:

$$K_{\mathrm{b}} = \frac{[HB+][OH-]}{[B]} \tag{6.3.1632}$$

where the concentrations are those at equilibrium. Again, we do not include [H_2O] in the equation because water is the solvent. The chemical reactions and ionization constants of the three bases shown are:

$$\begin{aligned} \mathrm{NO_2}^-(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{HNO_2}(aq) + \mathrm{OH}^-(aq) \qquad & K_{\mathrm{b}} &= 2.17 \times 10^{-11} \\ \mathrm{CH_3CO_2}^-(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{CH_3CO_2H}(aq) + \mathrm{OH}^-(aq) \qquad & K_{\mathrm{b}} &= 5.6 \times 10^{-10} \\ \mathrm{NH_3}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{NH_4}^+(aq) + \mathrm{OH}^-(aq) \qquad & K_{\mathrm{b}} &= 1.8 \times 10^{-5} \end{aligned} \tag{6.3.1633}$$

A table of ionization constants of weak bases appears in Table E2. As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

Consider the ionization reactions for a conjugate acid-base pair, $\mathrm{HA} - \mathrm{A}^-$:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{A}^-(aq) \tag{6.3.1634}$$

with $K_{\mathrm{a}} = \frac{[H3O+][A-]}{[HA]}$.

$$\mathrm{A}^-(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OH}^-(aq) + \mathrm{HA}(aq) \tag{6.3.1635}$$

with $K_{\mathrm{b}} = \frac{[HA][OH]}{[A-]}$.

Adding these two chemical equations yields the equation for the autoionization for water:

$$\begin{gathered} \cancel{\mathrm{HA}(aq)} + \mathrm{H_2O}(l) + \cancel{\mathrm{A}^-(aq)} + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \cancel{\mathrm{A}^-(aq)} + \mathrm{OH}^-(aq) + \cancel{\mathrm{HA}(aq)} \\ 2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{OH}^-(aq) \end{gathered}$$

As shown in the previous chapter on equilibrium, the K expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations' K expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that:

$$K_{\mathrm{a}} \times K_{\mathrm{b}} = \frac{[H3O+][A-]}{[HA]} \times \frac{[HA][OH-]}{[A-]} = [\mathrm{H_3O}^+][\mathrm{OH}^-\,] = K_{\mathrm{w}} \tag{6.3.1636}$$

For example, the acid ionization constant of acetic acid (CH_3COOH) is 1.8 × 10^{-5}, and the base ionization constant of its conjugate base, acetate ion ($\mathrm{CH_3COO}^-$), is 5.6 × 10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_{\mathrm{a}} \times K_{\mathrm{b}} = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_{\mathrm{w}} \tag{6.3.1637}$$

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base, A^-, of the acid. If A^- is a strong base, any protons that are donated to water molecules are recaptured by A^-. Thus there is relatively little A^- and $\mathrm{H_3O}^+$ in solution, and the acid, HA, is weak. If A^- is a weak base, water binds the protons more strongly, and the solution contains primarily A^- and $\mathrm{H_3O}^+$—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure 6.3.2).

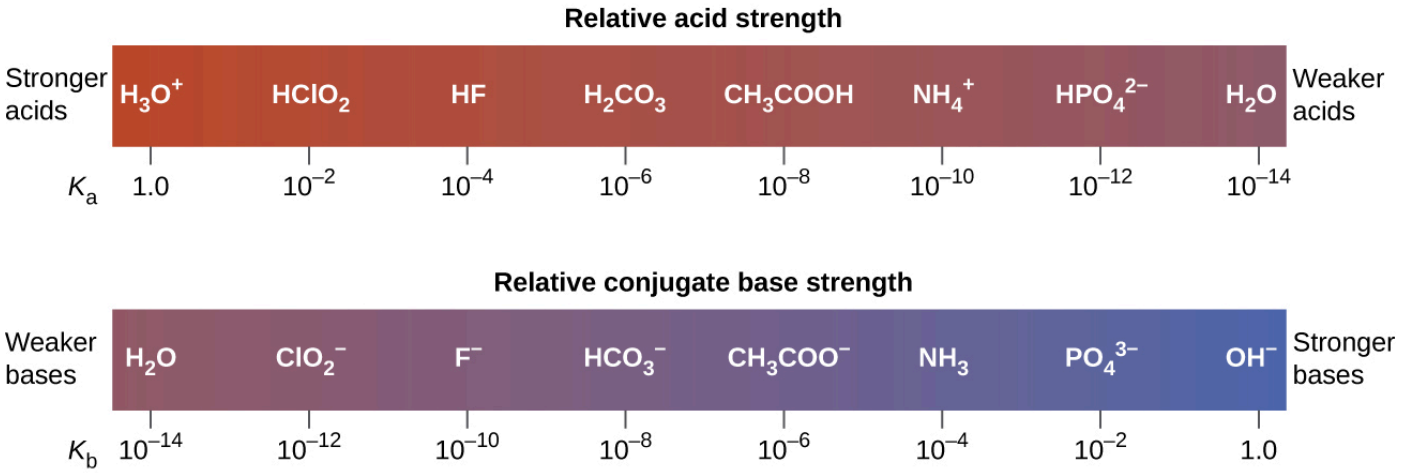


Figure 6.3.2: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure 6.3.3 lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.

The first six acids in Figure 6.3.3 are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure 6.3.3 form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure 6.3.3 exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

Acid			Base		
perchloric acid	$HClO_4$	Undergo complete acid ionization in water	Do not undergo base ionization in water	ClO_4^-	perchlorate ion
sulfuric acid	H_2SO_4			HSO_4^-	hydrogen sulfate ion
hydrogen iodide	HI			I^-	iodide ion
hydrogen bromide	HBr			Br^-	bromide ion
hydrogen chloride	HCl			Cl^-	chloride ion
nitric acid	HNO_3			NO_3^-	nitrate ion
hydronium ion	H_3O^+			H_2O	water
hydrogen sulfate ion	HSO_4^-			SO_4^{2-}	sulfate ion
phosphoric acid	H_3PO_4			$H_2PO_4^-$	dihydrogen phosphate ion
hydrogen fluoride	HF			F^-	fluoride ion
nitrous acid	HNO_2			NO_2^-	nitrite ion
acetic acid	CH_3CO_2H			$CH_3CO_2^-$	acetate ion
carbonic acid	H_2CO_3			HCO_3^-	hydrogen carbonate ion
hydrogen sulfide	H_2S			HS^-	hydrogen sulfide ion
ammonium ion	NH_4^+			HN_3	ammonia
hydrogen cyanide	HCN			CN^-	cyanide ion
hydrogen carbonate ion	HCO_3^-			CO_3^{2-}	carbonate ion
water	H_2O			OH^-	hydroxide ion
hydrogen sulfide ion	HS^-	Do not undergo acid ionization in water	Undergo complete base ionization in water	S^{2-}	sulfide ion
ethanol	C_2H_5OH			$C_2H_5O^-$	ethoxide ion
ammonia	NH_3			NH_2^-	amide ion
hydrogen	H_2			H^-	hydride ion
methane	CH_4			CH_3^-	methide ion

Increasing acid strength

Increasing base strength

Figure 6.3.3: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure 6.3.3. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

Example 6.3.2: The Product $K_a \times K_b = K_w$

Use the K_b for the nitrite ion, NO_2^-, to calculate the K_a for its conjugate acid.

Solution

K_b for NO_2^- is given in this section as 2.17×10^{-11}. The conjugate acid of NO_2^- is HNO_2; K_a for HNO_2 can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_a, we get:

$$\begin{aligned} K_a &= \frac{K_w}{K_b} \\ &= \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}} \\ &= 4.6 \times 10^{-4} \end{aligned}$$

This answer can be verified by finding the K_a for HNO_2 in Table E1

Exercise 6.3.2

We can determine the relative acid strengths of NH_4^+ and HCN by comparing their ionization constants. The ionization constant of HCN is given in Table E1 as 4.9×10^{-10}. The ionization constant of NH_4^+ is not listed, but the ionization constant of its conjugate base, NH_3, is listed as 1.8×10^{-5}. Determine the ionization constant of NH_4^+, and decide which is the stronger acid, HCN or NH_4^+.

Answer

NH_4^+ is the slightly stronger acid (K_a for $NH_4^+ = 5.6 \times 10^{-10}$).

Summary

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion.

Key Equations

- $K_a = \frac{[H3O+][A-]}{[HA]}$
- $K_b = \frac{[HB+][OH-]}{[B]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w$ (at room temperature)

Glossary

acid ionization constant (K_a)
: equilibrium constant for the ionization of a weak acid

base ionization constant (K_b)
: equilibrium constant for the ionization of a weak base

leveling effect of water
: any acid stronger than H_3O^+, or any base stronger than OH^- will react with water to form H_3O^+, or OH^-, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

percent ionization
: ratio of the concentration of the ionized acid to the initial acid concentration, times 100

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VI: ACID–BASE EQUILIBRIA

Acids and bases have been defined differently by three sets of theories. One is the Arrhenius definition, which revolves around the idea that acids are substances that ionize (break off) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide (OH^-) ions in solution. On the other hand, the Bronsted-Lowry definition defines acids as substances that donate protons (H^+) whereas bases are substances that accept protons. Also, the Lewis theory of acids and bases states that acids are electron pair acceptors while bases are electron pair donors. Acids and bases can be defined by their physical and chemical observations.

6.1: Classifications of Acids and Bases

6.2: The Brønsted-Lowry Scheme

6.3: Acid and Base Strength

6.4: Equilibria Involving Weak Acids and Bases

6.5: Buffer Solutions

6.6: Acid-Base Titration Curves

6.7: Polyprotic Acids

6.8: A Deeper Look - Exact Treatment of Acid-Base Equilibria

6.9: Organic Acids and Bases - Structure and Reactivity

6.10: Lewis Bases as Nucleophilic Reactants in Organic Reactions

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6.4: Equilibria Involving Weak Acids and Bases

Learning Objectives

- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid, with the nonionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid ($\mathrm{CH_3CO_2H}$) is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)$$

giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules. We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment (Figure 6.4.1). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

$$K_\mathrm{a} = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]} = 1.8 \times 10^{-5}$$



Figure 6.4.1: pH paper indicates that a 0.1-M solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[\mathrm{H_3O^+}]$ = 0.1 M. A 0.1-M solution of CH_3CO_2H (beaker on right) has a pH of 3 ($[\mathrm{H_3O^+}]$ = 0.001 M) because the weak acid CH_3CO_2H is only partially ionized. In this solution, $[\mathrm{H_3O^+}] < [\mathrm{CH_3CO_2H}]$. (credit: modification of work by Sahar Atwa)

Table 6.4.1: Ionization Constants of Some Weak Acids

Ionization Reaction	K_a at 25 °C
$\mathrm{HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}}$	1.2×10^{-2}

Ionization Reaction	K_a at 25 °C
$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	3.5×10^{-4}
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	4.6×10^{-4}
$HNCO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	2×10^{-4}
$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$	1.8×10^{-4}
$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$	1.8×10^{-5}
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	2.9×10^{-8}
$HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-$	2.8×10^{-9}
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9×10^{-10}

Table 6.4.1 gives the ionization constants for several weak acids; additional ionization constants can be found in Table E1.

At equilibrium, a solution of a weak base in water is a mixture of the nonionized base, the conjugate acid of the weak base, and hydroxide ion with the nonionized base present in the greatest concentration. Thus, a weak base increases the hydroxide ion concentration in an aqueous solution (but not as much as the same amount of a strong base).

For example, a solution of the weak base trimethylamine, $(CH_3)_3N$, in water reacts according to the equation:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$$

This gives an equilibrium mixture with most of the base present as the nonionized amine. This equilibrium is analogous to that described for weak acids.

We can confirm by measuring the pH of an aqueous solution of a weak base of known concentration that only a fraction of the base reacts with water (Figure 6.4.2). The remaining weak base is present as the unreacted form. The equilibrium constant for the ionization of a weak base, K_b, is called the **ionization constant** of the weak base, and is equal to the reaction quotient when the reaction is at equilibrium. For trimethylamine, at equilibrium:

$$K_b = \frac{[(CH3)3NH+][OH-]}{[(CH3)3N]}$$



Figure 6.4.2: pH paper indicates that a 0.1-M solution of NH_3 (left) is weakly basic. The solution has a pOH of 3 ($[OH^-]$ = 0.001 M) because the weak base NH_3 only partially reacts with water. A 0.1-M solution of NaOH (right) has a pOH of 1 because NaOH is a strong base (credit: modification of work by Sahar Atwa).

The ionization constants of several weak bases are given in Table 6.4.2 and Table E2.

Table 6.4.2: Ionization Constants of Some Weak Bases

Ionization Reaction	K_b at 25 °C
$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$	5.9×10^{-4}
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.4×10^{-4}
$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$	6.3×10^{-5}
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
$C_6H_5NH_2 + H_2O \rightleftharpoons C_6N_5NH_3^+ + OH^-$	4.3×10^{-10}

Example 6.4.3: Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar; that's why it tastes sour. At equilibrium, a solution contains $[CH_3CO_2H]$ = 0.0787 *M* and $[H_3O^+] = [CH_3CO_2^-] = 0.00118\ M$. What is the value of K_a for acetic acid?



Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by "HomeSpot HQ"/Flickr)

Solution

We are asked to calculate an equilibrium constant from equilibrium concentrations. At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)$$

$$K_\mathrm{a} = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]}$$

$$= \frac{(0.00118)(0.00118)}{0.0787}$$

$$= 1.77 \times 10^{-5}$$

Exercise 6.4.3

What is the equilibrium constant for the ionization of the $\mathrm{HSO_4^-}$ ion, the weak acid used in some household cleansers:

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq)$$

In one mixture of $NaHSO_4$ and Na_2SO_4 at equilibrium, $[\mathrm{H_3O^+}] = 0.027\ M$; $[\mathrm{HSO_4^-}] = 0.29\ M$; and $[\mathrm{SO_4^{2-}}] = 0.13\ M$.

Answer

K_a for $\mathrm{HSO_4^-} = 1.2 \times \times 10^{-2}$

Example 6.4.4: Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2] = 0.050\ M$, $[\mathrm{C_8H_{10}N_4O_2H^+}] = 5.0 \times 10^{-3}\ M$, and $[OH^-] = 2.5 \times 10^{-3}\ M$?

Solution

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$\mathrm{C_8H_{10}N_4O_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{C_8H_{10}N_4O_2H^+}(aq) + \mathrm{OH^-}(aq)$$

so

$$K_\mathrm{b} = \frac{[C8H10N4O2H+][OH-]}{[C8H10N4O2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

Exercise 6.4.4

What is the equilibrium constant for the ionization of the $\mathrm{HPO_4^{2-}}$ ion, a weak base:

$$\mathrm{HPO_4^{2-}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2PO_4^-}(aq) + \mathrm{OH^-}(aq)$$

In a solution containing a mixture of $\mathrm{NaH_2PO_4}$ and $\mathrm{Na_2HPO_4}$ at equilibrium with:

- $[\mathrm{OH^-}] = 1.3 \times 10^{-6} M$
- $[\mathrm{H_2PO_4^-}]$=0.042 M and
- $[\mathrm{HPO_4^{2-}}]$=0.341 M.

Answer

K_b for $\mathrm{HPO_4^{2-}} = 1.6 \times 10^{-7}$

Example 6.4.5: Determination of K_a or K_b from pH

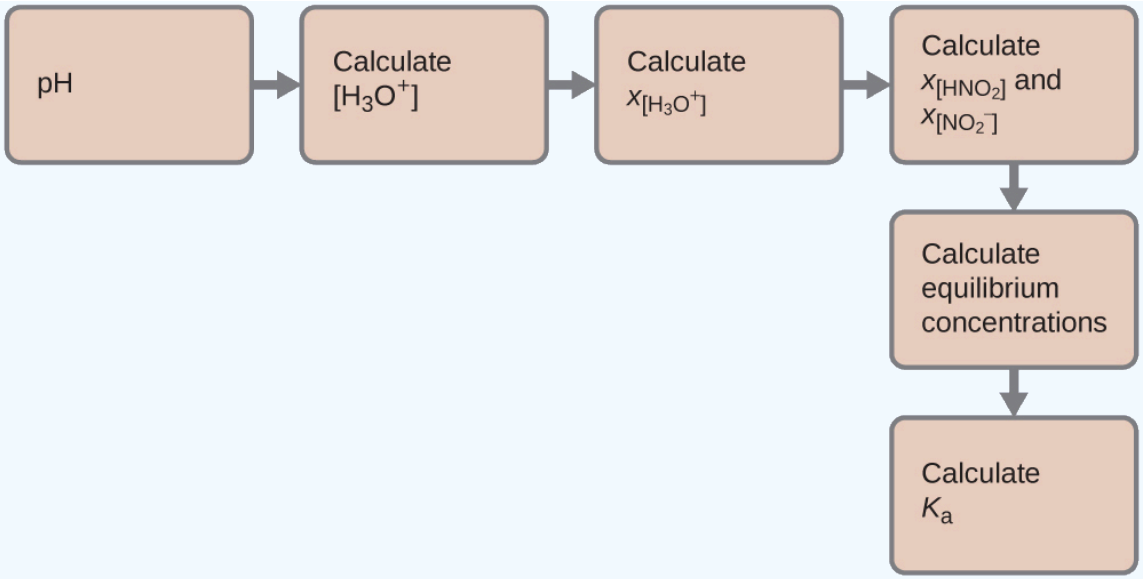
The pH of a 0.0516-*M* solution of nitrous acid, $\mathrm{HNO_2}$, is 2.34. What is its K_a?

$$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{NO_2^-}(aq)$$

Solution

We determine an equilibrium constant starting with the initial concentrations of $\mathrm{HNO_2}$, $\mathrm{H_3O^+}$, and $\mathrm{NO_2^-}$ as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the concentration of hydronium ion.)

We can solve this problem with the following steps in which *x* is a change in concentration of a species in the reaction:



We can summarize the various concentrations and changes as shown here (the concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its concentration):

	HNO_2 + H_2O ⇌ H_3O^+ + NO_2^-			
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	$-x$	+	x	x
Equilibrium concentration (*M*)	$[HNO_2]_i + (-x) = 0.0516 + (-x)$		$[H_3O]^+ + x$ $[NO_2]^- + x$ ~0 + x	0.0046

To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate $[\mathrm{H_3O^+}]$, the equilibrium concentration of $\mathrm{H_3O^+}$, from the pH:

$$[\mathrm{H_3O^+}] = 10^{-2.34} = 0.0046\ M$$

The change in concentration of $\mathrm{H_3O^+}$, $x_{[\mathrm{H_3O^+}]}$, is the difference between the equilibrium concentration of H_3O^+, which we determined from the pH, and the initial concentration, $[\mathrm{H_3O^+}]_i$. The initial concentration of $\mathrm{H_3O^+}$ is its concentration in pure water, which is so much less than the final concentration that we approximate it as zero (~0).

The change in concentration of $\mathrm{NO_2^-}$ is equal to the change in concentration of $[\mathrm{H_3O^+}]$. For each 1 mol of $\mathrm{H_3O^+}$ that forms, 1 mol of $\mathrm{NO_2^-}$ forms. The equilibrium concentration of HNO_2 is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

	HNO_2 + H_2O ⇌ H_3O^+ + NO_2^-			
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	$-x$	+	x = 0.0046	x = 0.0046
Equilibrium concentration (*M*)	0.0470		0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H3O+][NO2-]}{[HNO2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

Exercise 6.4.5

The pH of a solution of household ammonia, a 0.950-*M* solution of NH_3, is 11.612. What is K_b for NH_3.

Answer

$$K_b = 1.8 \times 10^{-5}$$

Example 6.4.6: Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid, HCO_2H, is the irritant that causes the body's reaction to ant stings.



The pain of an ant's sting is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH in a 0.534-*M* solution of formic acid?

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq) \quad K_a = 1.8 \times 10^{-4}$$

Solution

1. Determine x and equilibrium concentrations. The equilibrium expression is:

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq)$$

The concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its change in concentration when setting up the ICE table.

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

	HCO_2H +	H_2O ⇌	H_3O^+
Initial concentration (*M*)	0.534	~0	0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.534 + (-x)$	$0 + x = x$	$0 + x = x$

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_a = 1.8 \times 10^{-4} = \frac{[H3O+][HCO2-]}{[HCO2H]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

Now solve for x. Because the initial concentration of acid is reasonably large and K_a is very small, we assume that $x << 0.534$, which *permits* us to simplify the denominator term as $(0.534 - x) = 0.534$. This gives:

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solve for x as follows:

$$x^2 = 0.534 \times (1.8 \times 10^{-4})$$

$$= 9.6 \times 10^{-5}$$

$$x = \sqrt{9.6 \times 10^{-5}}$$

$$= 9.8 \times 10^{-3}$$

To check the assumption that x is small compared to 0.534, we calculate:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534}$$

$$= 1.8 \times 10^{-2} \, (1.8$$

x is less than 5% of the initial concentration; the assumption is valid.

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change

in that concentration as indicated in the last line of the table:

$$[\mathrm{H_3O^+}] = \ 0 + x = 0 + 9.8 \times 10^{-3}\ M.$$
$$= 9.8 \times 10^{-3}\ M$$

The pH of the solution can be found by taking the negative log of the $[\mathrm{H_3O^+}]$, so:

$$pH = -\log(9.8 \times 10^{-3}) = 2.01$$

Exercise 6.4.6: acetic acid

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \quad K_\mathrm{a} = 1.8 \times 10^{-5}$$

Hint

Determine $[\mathrm{CH_3CO_2^-}]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or $\frac{[CH3CO2-]}{[CH3CO2H]_{initial}} \times 100$.

Answer

percent ionization = 1.3%

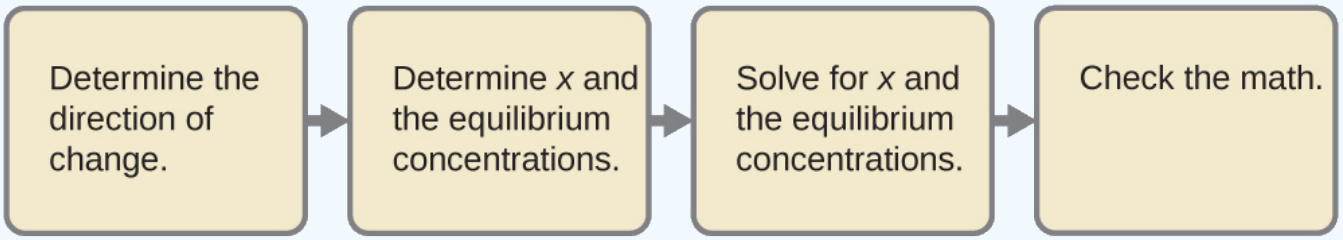
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

Example 6.4.7: Equilibrium Concentrations in a Solution of a Weak Base

Find the concentration of hydroxide ion in a 0.25-*M* solution of trimethylamine, a weak base:

$$(\mathrm{CH_3})_3\mathrm{N}(aq) + \mathrm{H_2O}(l) \rightleftharpoons (\mathrm{CH_3})_3\mathrm{NH^+}(aq) + \mathrm{OH^-}(aq) \quad K_\mathrm{b} = 6.3 \times 10^{-5}$$

Solution This problem requires that we calculate an equilibrium concentration by determining concentration changes as the ionization of a base goes to equilibrium. The solution is approached in the same way as that for the ionization of formic acid in Example 6.4.6. The reactants and products will be different and the numbers will be different, but the logic will be the same:



1. Determine x and equilibrium concentrations. The table shows the changes and concentrations:

	$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$			
Initial concentration (*M*)	0.25		0	~0
Change (*M*)	$-x$		x	x
Equilibrium concentration (*M*)	0.25 + (−*x*)		0 + *x*	~0 + *x*

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_b = \frac{[(CH3)3NH+][OH-]}{[(CH3)3N]} = \frac{(x)(x)}{0.25 - x =} 6.3 \times 10^{-5}$$

If we assume that *x* is small relative to 0.25, then we can replace (0.25 – *x*) in the preceding equation with 0.25. Solving the simplified equation gives:

$$x = 4.0 \times 10^{-3}$$

This change is less than 5% of the initial concentration (0.25), so the assumption is justified.

Recall that, for this computation, x is equal to the equilibrium concentration of *hydroxide ion* in the solution (see earlier tabulation):

$$([\mathrm{OH}^-] = \ 0 + x = x = 4.0 \times 10^{-3}\ M$$
$$= 4.0 \times 10^{-3}\ M$$

Then calculate pOH as follows:

$$\mathrm{pOH} = -\log(4.3 \times 10^{-3}) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_\mathrm{w} = 14.00$$

permits the computation of pH:

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 2.37 = 11.60$$

Check the work. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

Exercise 6.4.7

a. Show that the calculation in Step 2 of this example gives an *x* of 4.3×10^{-3} and the calculation in Step 3 shows $K_b = 6.3 \times 10^{-5}$.

b. Find the concentration of hydroxide ion in a 0.0325-*M* solution of ammonia, a weak base with a K_b of 1.76×10^{-5}. Calculate the percent ionization of ammonia, the fraction ionized × 100, or $\frac{[NH4+]}{[NH3]} \times 100\%$

Answer a

$7.56 \times 10^{-4}\ M$, 2.33%

Answer b

2.33%

Some weak acids and weak bases ionize to such an extent that the simplifying assumption that *x* is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

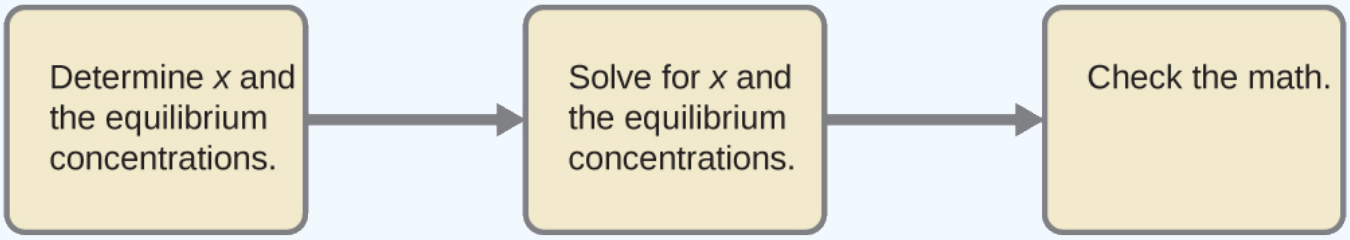
Example 6.4.8: Equilibrium Concentrations in a Solution of a Weak Acid

Sodium bisulfate, $NaHSO_4$, is used in some household cleansers because it contains the HSO_4^- ion, a weak acid. What is the pH of a 0.50-*M* solution of HSO_4^-?

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \quad K_a = 1.2 \times 10^{-2}$$

Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of HSO_4^- so that we can use $[H_3O^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



1. Determine x and equilibrium concentrations. This table shows the changes and concentrations:

	HSO_4^- + H_2O ⇌ H_3O^+ + SO_4^{2-}			
Initial concentration (*M*)	0.50		~0	0
Change (*M*)	$-x$		x	x
Equilibrium concentration (*M*)	$0.50 + (-x) = 0.50 - x$		$0 + x = x$	$0 + x = x$

2. Solve for x and the concentrations.

As we begin solving for x, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of x.

At equilibrium:

$$K_{\mathrm{a}} = 1.2 \times 10^{-2} = \frac{[H3O+][SO4^{2}-]}{[HSO4-]} = \frac{(x)(x)}{0.50 - x}$$

If we assume that *x* is small and approximate (0.50 – *x*) as 0.50, we find:

$$x = 7.7 \times 10^{-2}$$

When we check the assumption, we confirm:

$$\frac{x}{[\mathrm{HSO}_4^-]_{\mathrm{i}}} \overset{?}{\leq} 0.05$$

which for this system is

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15(15\%)$$

The value of x is not less than 5% of 0.50, so the assumption is not valid. We need the quadratic formula to find x.

The equation:

$$K_{\mathrm{a}} = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

gives

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2}x = x^{2+}$$

or

$$x^{2+} + 1.2 \times 10^{-2}x - 6.0 \times 10^{-3} = 0$$

This equation can be solved using the quadratic formula. For an equation of the form

$$ax^{2+} + bx + c = 0,$$

x is given by the quadratic equation:

$$x = \frac{-b \pm \sqrt{b^{2+} - 4ac}}{2a}$$

In this problem, $a = 1$, $b = 1.2 \times 10^{-3}$, and $c = -6.0 \times 10^{-3}$.

Solving for x gives a negative root (which cannot be correct since concentration cannot be negative) and a positive root:

$$x = 7.2 \times 10^{-2}$$

Now determine the hydronium ion concentration and the pH:

$$[\mathrm{H_3O^+}] = \ 0 + x = 0 + 7.2 \times 10^{-2}\ M$$
$$= 7.2 \times 10^{-2}\ M$$

The pH of this solution is:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log 7.2 \times 10^{-2} = 1.14$$

Exercise 6.4.8

a. Show that the quadratic formula gives $x = 7.2 \times 10^{-2}$.
b. Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$\mathrm{C_8H_{10}N_4O_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{C_8H_{10}N_4O_2H^+}(aq) + \mathrm{OH^-}(aq) \quad K_\mathrm{b} = 2.5 \times 10^{-4}$$

Hint

It will be necessary to convert [OH^-] to $[\mathrm{H_3O^+}]$ or pOH to pH toward the end of the calculation.

Answer

pH 11.16

The Relative Strengths of Strong Acids and Bases

Strong acids, such as HCl, HBr, and HI, all exhibit the same strength in water. The water molecule is such a strong base compared to the conjugate bases Cl^-, Br^-, and I^- that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find HCl, HBr, and HI differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol (a weaker base than water), the extent of ionization increases in the order $\mathrm{HCl} < \mathrm{HBr} < \mathrm{HI}$, and so HI is demonstrated to be the strongest of these acids. The inability to discern differences in strength among strong acids dissolved in water is known as the leveling effect of water.

Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, O^{2-}, and the amide ion, $\mathrm{NH_2^-}$, are such strong bases that they react completely with water:

$$\mathrm{O^{2-}}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{OH^-}(aq) + \mathrm{OH^-}(aq) \tag{6.4.1638}$$

$$\mathrm{NH_2^-}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{NH_3}(aq) + \mathrm{OH^-}(aq) \tag{6.4.1639}$$

Thus, O^{2-} and $\mathrm{NH_2^-}$ appear to have the same base strength in water; they both give a 100% yield of hydroxide ion.

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is $\mathrm{HF} < \mathrm{HCl} < \mathrm{HBr} < \mathrm{HI}$. Likewise, for group 16, the order of increasing acid strength is $H_2O < H_2S < H_2Se < H_2Te$. Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $\mathrm{CH_4} < \mathrm{NH_3} < \mathrm{H_2O} < \mathrm{HF}$; across the third row, it is $\mathrm{SiH_4} < \mathrm{PH_3} < \mathrm{H_2S} < \mathrm{HCl}$ (see Figure 6.4.3).

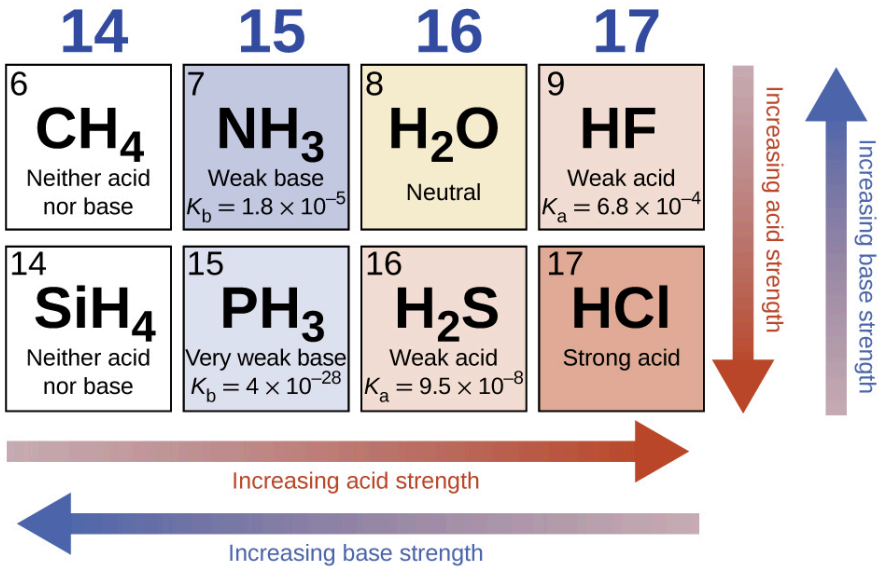
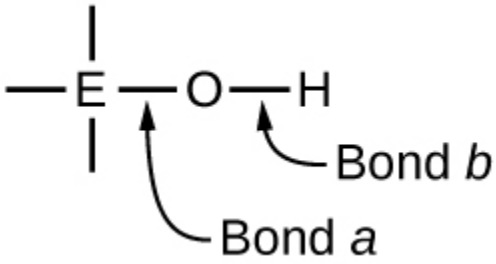


Figure 6.4.3: As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

Compounds containing oxygen and one or more hydroxyl (OH) groups can be acidic, basic, or amphoteric, depending on the position in the periodic table of the central atom E, the atom bonded to the hydroxyl group. Such compounds have the general formula $O_nE(OH)_m$, and include sulfuric acid, $O_2S(OH)_2$, sulfurous acid, $OS(OH)_2$, nitric acid, O_2NOH, perchloric acid, O_3ClOH, aluminum hydroxide, $Al(OH)_3$, calcium hydroxide, $Ca(OH)_2$, and potassium hydroxide, KOH:



If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic –OH groups that are called oxyacids.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3, or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure 6.4.4).

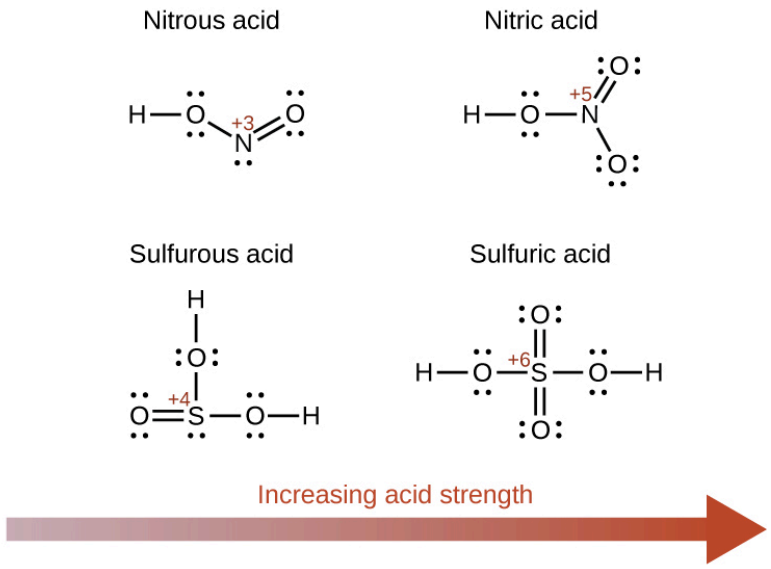


Figure 6.4.4: As the oxidation number of the central atom E increases, the acidity also increases.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate $\mathrm{Al(H_2O)_3(OH)_3}$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $\mathrm{Al(H_2O)_3(OH)_3}$, is converted into the soluble ion, $\mathrm{[Al(H_2O)_2(OH)_4]^-}$, by reaction with hydroxide ion:

$$\mathrm{[Al(H_2O)_3(OH)_3](\mathit{aq}) + OH^-(\mathit{aq}) \rightleftharpoons H_2O(\mathit{l}) + [Al(H_2O)_2(OH)_4]^-(\mathit{aq})}$$

In this reaction, a proton is transferred from one of the aluminum-bound H_2O molecules to a hydroxide ion in solution. The $\mathrm{Al(H_2O)_3(OH)_3}$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion $\mathrm{[Al(H_2O)_6]^{3+}}$ by reaction with hydronium ion:

$$\mathrm{3\,H_3O^+(\mathit{aq}) + Al(H_2O)_3(OH)_3(\mathit{aq}) \rightleftharpoons Al(H_2O)_6{}^{3+}(\mathit{aq}) + 3\,H_2O(\mathit{l})}$$

In this case, protons are transferred from hydronium ions in solution to $\mathrm{Al(H_2O)_3(OH)_3}$, and the compound functions as a base.

Summary

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion. The strengths of the binary acids increase from left to right across a period of the periodic table (CH_4 < NH_3 < H_2O < HF), and they increase down a group (HF < HCl < HBr < HI). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases (H_2SO_3 < H_2SO_4). The strengths of oxyacids also increase as the electronegativity of the central element increases [H_2SeO_4 < H_2SO_4].

Key Equations

- $K_\mathrm{a} = \dfrac{[H3O+][A-]}{[HA]}$
- $K_\mathrm{b} = \dfrac{[HB+][OH-]}{[B]}$

- $K_a \times K_b = 1.0 \times 10^{-14} = K_w$ (at room temperature)
- $\text{Percent ionization} = \dfrac{[H3O+]_{eq}}{[HA]_0} \times 100$

Glossary

acid ionization constant (K_a)
: equilibrium constant for the ionization of a weak acid

base ionization constant (K_b)
: equilibrium constant for the ionization of a weak base

leveling effect of water
: any acid stronger than $\mathrm{H_3O^+}$, or any base stronger than $\mathrm{OH^-}$ will react with water to form $\mathrm{H_3O^+}$, or $\mathrm{OH^-}$, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

oxyacid
: compound containing a nonmetal and one or more hydroxyl groups

percent ionization
: ratio of the concentration of the ionized acid to the initial acid concentration, times 100

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6.5: Buffer Solutions

Learning Objectives

- To understand how adding a common ion affects the position of an acid–base equilibrium.
- To know how to use the Henderson-Hasselbalch approximation to calculate the pH of a buffer.

Buffers are solutions that maintain a relatively constant pH when an acid or a base is added. They therefore protect, or "buffer," other molecules in solution from the effects of the added acid or base. Buffers contain either a weak acid (HA) and its conjugate base (A^-) or a weak base (B) and its conjugate acid (BH^+), and they are critically important for the proper functioning of biological systems. In fact, every biological fluid is buffered to maintain its physiological pH.

The Common Ion Effect: Weak Acids Combined with Conjugate Bases

To understand how buffers work, let's look first at how the ionization equilibrium of a weak acid is affected by adding either the conjugate base of the acid or a strong acid (a source of $\mathrm{H^+}$). Le Chatelier's principle can be used to predict the effect on the equilibrium position of the solution. A typical buffer used in biochemistry laboratories contains acetic acid and a salt such as sodium acetate. The dissociation reaction of acetic acid is as follows:

[redacted]

and the equilibrium constant expression is as follows:

[redacted]

Sodium acetate ($\mathrm{CH_3CO_2Na}$) is a strong electrolyte that ionizes completely in aqueous solution to produce $\mathrm{Na^+}$ and $\mathrm{CH_3CO_2^-}$ ions. If sodium acetate is added to a solution of acetic acid, Le Chatelier's principle predicts that the equilibrium in Equation 1.1.1 will shift to the left, consuming some of the added $\mathrm{CH_3COO^-}$ and some of the $\mathrm{H^+}$ ions originally present in solution.

Because $\mathrm{Na^+}$ is a **spectator ion**, it has no effect on the position of the equilibrium and can be ignored. The addition of sodium acetate produces a new equilibrium composition, in which $[\mathrm{H^+}]$ is less than the initial value. Because $[\mathrm{H^+}]$ has decreased, the pH will be higher. Thus adding a salt of the conjugate base to a solution of a weak acid increases the pH. This makes sense because sodium acetate is a base, and adding any base to a solution of a weak acid should increase the pH.

If we instead add a strong acid such as HCl to the system, $[\mathrm{H^+}]$ increases. Once again the equilibrium is temporarily disturbed, but the excess $\mathrm{H^+}$ ions react with the conjugate base ($\mathrm{CH_3CO_2^-}$), whether from the parent acid or sodium acetate, to drive the equilibrium to the left. The net result is a new equilibrium composition that has a lower [$\mathrm{CH_3CO_2^-}$] than before. In both cases, only the equilibrium composition has changed; the ionization constant K_a for acetic acid remains the same. Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium, in this case $\mathrm{CH_3CO_2^-}$, will therefore shift the equilibrium in the direction that reduces the concentration of the common ion. The shift in equilibrium is via the common ion effect.

> Adding a common ion to a system at equilibrium affects the equilibrium composition, but not the ionization constant.

Example 6.5.1

A 0.150 M solution of formic acid at 25°C (pKa = 3.75) has a pH of 2.28 and is 3.5% ionized.

a. Is there a change to the pH of the solution if enough solid sodium formate is added to make the final formate concentration 0.100 M (assume that the formic acid concentration does not change)?
b. What percentage of the formic acid is ionized if 0.200 M HCl is added to the system?

Given: solution concentration and pH, pK_a, and percent ionization of acid; final concentration of conjugate base or strong acid added

Asked for: pH and percent ionization of formic acid

Strategy:

A. Write a balanced equilibrium equation for the ionization equilibrium of formic acid. Tabulate the initial concentrations, the changes, and the final concentrations.
B. Substitute the expressions for the final concentrations into the expression for Ka. Calculate $[\mathrm{H}^+]$ and the pH of the solution.
C. Construct a table of concentrations for the dissociation of formic acid. To determine the percent ionization, determine the anion concentration, divide it by the initial concentration of formic acid, and multiply the result by 100.

Solution:

A Because sodium formate is a strong electrolyte, it ionizes completely in solution to give formate and sodium ions. The Na^+ ions are spectator ions, so they can be ignored in the equilibrium equation. Because water is both a much weaker acid than formic acid and a much weaker base than formate, the acid–base properties of the solution are determined solely by the formic acid ionization equilibrium:

$$\mathrm{HCO_2H\,(aq) \rightleftharpoons HCO_2^-\,(aq) + H^+\,(aq)}$$

The initial concentrations, the changes in concentration that occur as equilibrium is reached, and the final concentrations can be tabulated.

Final Concentration

ICE	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
Initial	0.150	1.00×10^{-7}	0.100
Change	–x	+x	+x
Equilibrium	(0.150 – x)	x	(0.100 + x)

B We substitute the expressions for the final concentrations into the equilibrium constant expression and make our usual simplifying assumptions, so

$$\begin{aligned} K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} &= \frac{(x)(0.100+x)}{0.150-x} \\ &\approx \frac{x(0.100)}{0.150} \\ &\approx 10^{-3.75} \\ &\approx 1.8 \times 10^{-4} \end{aligned}$$

Rearranging and solving for x,

$$\begin{aligned} x &= (1.8 \times 10^{-4}) \times \frac{0.150\ M}{0.100\ M} \\ &= 2.7 \times 10^{-4} \\ &= [H^+] \end{aligned}$$

The value of x is small compared with 0.150 or 0.100 M, so our assumption about the extent of ionization is justified. Moreover,

$$K_aC_{HA} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5}$$

which is greater than 1.0×10^{-6}, so again, our assumption is justified. The final pH is:

$$pH = -\log(2.7 \times 10^{-4}) = 3.57$$

compared with the initial value of 2.29. Thus adding a salt containing the conjugate base of the acid has increased the pH of the solution, as we expect based on Le Chatelier's principle; the stress on the system has been relieved by the consumption of $\mathrm{H^+}$ ions, driving the equilibrium to the left.

C Because HCl is a strong acid, it ionizes completely, and chloride is a spectator ion that can be neglected. Thus the only relevant acid–base equilibrium is again the dissociation of formic acid, and initially the concentration of formate is zero. We can construct a table of initial concentrations, changes in concentration, and final concentrations.

$$HCO_2H(aq) \leftrightharpoons H^+(aq) + HCO_2^-(aq)$$

initial concentrations, changes in concentration, and final concentrations

	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
initial	0.150	0.200	0
change	–x	+x	+x
final	(0.150 – x)	(0.200 + x)	x

To calculate the percentage of formic acid that is ionized under these conditions, we have to determine the final $[\mathrm{HCO_2^-}]$. We substitute final concentrations into the equilibrium constant expression and make the usual simplifying assumptions, so

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(0.200 + x)(x)}{0.150 - x} \approx \frac{x(0.200)}{0.150} = 1.80 \times 10^{-4}$$

Rearranging and solving for x,

$$x = (1.80 \times 10^{-4}) \times \frac{0.150\ M}{0.200\ M}$$
$$= 1.35 \times 10^{-4} = [HCO_2^-]$$

Once again, our simplifying assumptions are justified. The percent ionization of formic acid is as follows:

$$\text{percent ionization} = \frac{1.35 \times 10^{-4}\ M}{0.150\ M} \times 100\% = 0.0900\%$$

Adding the strong acid to the solution, as shown in the table, decreased the percent ionization of formic acid by a factor of approximately 38 (3.45%/0.0900%). Again, this is consistent with Le Chatelier's principle: adding $\mathrm{H^+}$ ions drives the dissociation equilibrium to the left.

Exercise 6.5.1

A 0.225 M solution of ethylamine ($\mathrm{CH_3CH_2NH_2}$ with $pK_b = 3.19$) has a pH of 12.08 and a percent ionization of 5.4% at 20°C. Calculate the following:

a. the pH of the solution if enough solid ethylamine hydrochloride ($\mathrm{EtNH_3Cl}$) is added to make the solution 0.100 M in $\mathrm{EtNH_3^+}$
b. the percentage of ethylamine that is ionized if enough solid NaOH is added to the original solution to give a final concentration of 0.050 M NaOH

Answer a

11.16

Answer b

1.3%

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A Video Discussing the Common Ion Effect: The Common Ion Effecr(opens in new window) [youtu.be]

The Common Ion Effect: Weak Bases Combined with Conjugate Acids

Now let's suppose we have a buffer solution that contains equimolar concentrations of a weak base (B) and its conjugate acid (BH^+). The general equation for the ionization of a weak base is as follows:

If the equilibrium constant for the reaction as written in Equation 1.1.5 is small, for example $K_b = 10^{-5}$, then the equilibrium constant for the reverse reaction is very large: $K = \frac{1}{K_b} = 10^5$. Adding a strong base such as OH^- to the solution therefore causes the equilibrium in Equation 1.1.5 to shift to the left, consuming the added OH^-. As a result, the OH^- ion concentration in solution remains relatively constant, and the pH of the solution changes very little. Le Chatelier's principle predicts the same outcome: when the system is stressed by an increase in the OH^- ion concentration, the reaction will proceed to the left to counteract the stress.

If the pK_b of the base is 5.0, the pK_a of its conjugate acid is

$$pK_a = pK_w - pK_b = 14.0–5.0 = 9.0.$$

Thus the equilibrium constant for ionization of the conjugate acid is even smaller than that for ionization of the base. The ionization reaction for the conjugate acid of a weak base is written as follows:

[redacted]

Again, the equilibrium constant for the reverse of this reaction is very large: $K = 1/K_a = 10^9$. If a strong acid is added, it is neutralized by reaction with the base as the reaction in Equation 2.1.969 shifts to the left. As a result, the H^+ ion concentration does not increase very much, and the pH changes only slightly. In effect, a buffer solution behaves somewhat like a sponge that can absorb H^+ and OH^- ions, thereby preventing large changes in pH when appreciable amounts of strong acid or base are added to a solution.

Buffers are characterized by the pH range over which they can maintain a more or less constant pH and by their buffer capacity, the amount of strong acid or base that can be absorbed before the pH changes significantly. Although the useful pH range of a buffer depends strongly on the chemical properties of the weak acid and weak base used to prepare the buffer (i.e., on K), its buffer capacity depends solely on the concentrations of the species in the buffered solution. The more concentrated the buffer solution, the greater its buffer capacity. As illustrated in Figure 6.5.1, when $NaOH$ is added to solutions that contain different concentrations of an acetic acid/sodium acetate buffer, the observed change in the pH of the buffer is inversely proportional to the concentration of the buffer. If the buffer capacity is 10 times larger, then the buffer solution can absorb 10 times more strong acid or base before undergoing a significant change in pH.

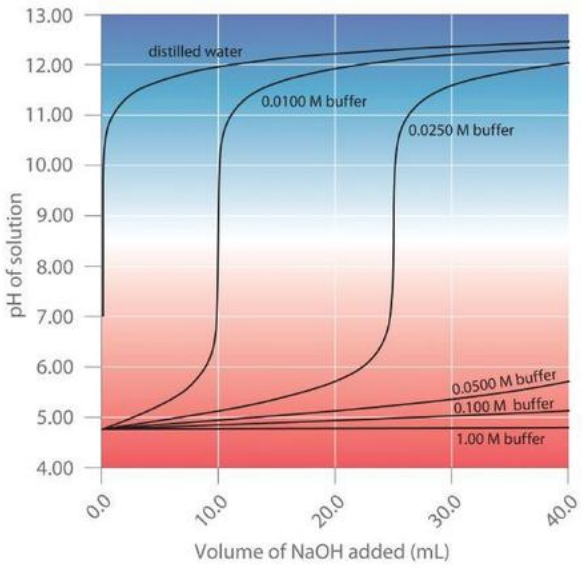


Figure 6.5.1: Effect of Buffer Concentration on the Capacity of a Buffer. (CC BY-SA-NC; Anonymous by request)

Graph of pH of solution against volume of NaOH added. Six different buffer concentrations are plotted.

A buffer maintains a relatively constant pH when acid or base is added to a solution. The addition of even tiny volumes of 0.10 M $NaOH$ to 100.0 mL of distilled water results in a very large change in pH. As the concentration of a 50:50 mixture of sodium acetate/acetic acid buffer in the solution is increased from 0.010 M to 1.00 M, the change in the pH produced by the addition of the same volume of $NaOH$ solution decreases steadily. For buffer concentrations of at least 0.500 M, the addition of even 25 mL of the $NaOH$ solution results in only a relatively small change in pH.

Calculating the pH of a Buffer

The pH of a buffer can be calculated from the concentrations of the weak acid and the weak base used to prepare it, the concentration of the conjugate base and conjugate acid, and the pK_a or pK_b of the weak acid or weak base. The procedure is analogous to that used in Example 6.5.1 to calculate the pH of a solution containing known concentrations of formic acid and formate.

An alternative method frequently used to calculate the pH of a buffer solution is based on a rearrangement of the equilibrium equation for the dissociation of a weak acid. The simplified ionization reaction is $HA \leftrightharpoons H^+ + A^-$, for which the equilibrium constant expression is as follows:

This equation can be rearranged as follows:

Taking the logarithm of both sides and multiplying both sides by –1,

Replacing the negative logarithms in Equation 5.2.1130,

or, more generally,

Equation 5.2.1131 and Equation 5.2.1132 are both forms of the Henderson-Hasselbalch approximation, named after the two early 20th-century chemists who first noticed that this rearranged version of the equilibrium constant expression provides an easy way to calculate the pH of a buffer solution. In general, the validity of the Henderson-Hasselbalch approximation may be limited to solutions whose concentrations are at least 100 times greater than their K_a values.

There are three special cases where the Henderson-Hasselbalch approximation is easily interpreted without the need for calculations:

- $[base] = [acid]$: Under these conditions,

  $$\frac{[base]}{[acid]} = 1$$

  in Equation 5.2.1132. Because $\log 1 = 0$,

  $$pH = pK_a$$

  regardless of the actual concentrations of the acid and base. Recall that this corresponds to the midpoint in the titration of a weak acid or a weak base.
- $[base]/[acid] = 10$: In Equation 5.2.1132, because $\log 10 = 1$,

  $$pH = pK_a + 1.$$
- $[base]/[acid] = 100$: In Equation 5.2.1132, because $\log 100 = 2$,

  $$pH = pK_a + 2.$$

Each time we increase the [base]/[acid] ratio by 10, the pH of the solution increases by 1 pH unit. Conversely, if the [base]/[acid] ratio is 0.1, then pH = pK_a – 1. Each additional factor-of-10 decrease in the [base]/[acid] ratio causes the pH to decrease by 1 pH unit.

> If [base] = [acid] for a buffer, then pH = pK_a. Changing this ratio by a factor of 10 either way changes the pH by ±1 unit.

Example 6.5.2

What is the pH of a solution that contains

a. 0.135 M HCO_2H and 0.215 M HCO_2Na? (The pK_a of formic acid is 3.75.)
b. 0.0135 M HCO_2H and 0.0215 M HCO_2Na?

c. 0.119 M pyridine and 0.234 M pyridine hydrochloride? (The pK_b of pyridine is 8.77.)

Given: concentration of acid, conjugate base, and pK_a; concentration of base, conjugate acid, and pK_b

Asked for: pH

Strategy:

Substitute values into either form of the Henderson-Hasselbalch approximation (Equations 5.2.1131 or 5.2.1132) to calculate the pH.

Solution:

According to the Henderson-Hasselbalch approximation (Equation 5.2.1131), the pH of a solution that contains both a weak acid and its conjugate base is

$$pH = pK_a + \log([A-]/[HA]).$$

A

Inserting the given values into the equation,

$$\begin{aligned} pH &= 3.75 + \log\left(\frac{0.215}{0.135}\right) \\ &= 3.75 + \log 1.593 \\ &= 3.95 \end{aligned}$$

This result makes sense because the $[A^-]/[HA]$ ratio is between 1 and 10, so the pH of the buffer must be between the pK_a (3.75) and $pK_a + 1$, or 4.75.

B

This is identical to part (a), except for the concentrations of the acid and the conjugate base, which are 10 times lower. Inserting the concentrations into the Henderson-Hasselbalch approximation,

$$\begin{aligned} pH &= 3.75 + \log\left(\frac{0.0215}{0.0135}\right) \\ &= 3.75 + \log 1.593 \\ &= 3.95 \end{aligned}$$

This result is identical to the result in part (a), which emphasizes the point that the pH of a buffer depends only on the ratio of the concentrations of the conjugate base and the acid, not on the magnitude of the concentrations. Because the $[A^-]/[HA]$ ratio is the same as in part (a), the pH of the buffer must also be the same (3.95).

C

In this case, we have a weak base, pyridine (Py), and its conjugate acid, the pyridinium ion (HPy^+). We will therefore use Equation 5.2.1132, the more general form of the Henderson-Hasselbalch approximation, in which "base" and "acid" refer to the appropriate species of the conjugate acid–base pair. We are given [base] = [Py] = 0.119 M and $[acid] = [HPy^+] = 0.234\ M$. We also are given $pK_b = 8.77$ for pyridine, but we need pK_a for the pyridinium ion. Recall from Equation 16.23 that the pK_b of a weak base and the pK_a of its conjugate acid are related:

$$pK_a + pK_b = pK_w.$$

Thus pK_a for the pyridinium ion is $pK_w - pK_b = 14.00 - 8.77 = 5.23$. Substituting this pK_a value into the Henderson-Hasselbalch approximation,

$$\begin{aligned} pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \\ &= 5.23 + \log\left(\frac{0.119}{0.234}\right) \\ &= 5.23 - 0.294 \\ &= 4.94 \end{aligned}$$

Once again, this result makes sense: the $[B]/[BH^+]$ ratio is about 1/2, which is between 1 and 0.1, so the final pH must be between the pK_a (5.23) and $pK_a - 1$, or 4.23.

Exercise 6.5.2

What is the pH of a solution that contains

a. 0.333 M benzoic acid and 0.252 M sodium benzoate?
b. 0.050 M trimethylamine and 0.066 M trimethylamine hydrochloride?

The pK_a of benzoic acid is 4.20, and the pK_b of trimethylamine is also 4.20.

Answer a

4.08

Answer b

9.68

YouTube Video

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https://www.youtube.com/embed/kGQDtZfletg?vq=hd1080

A Video Discussing Using the Henderson Hasselbalch Equation: Using the Henderson Hasselbalch Equation(opens in new window) [youtu.be] (opens in new window)

The Henderson-Hasselbalch approximation ((Equation 5.2.1131) can also be used to calculate the pH of a buffer solution after adding a given amount of strong acid or strong base, as demonstrated in Example 6.5.3.

Example 6.5.3

The buffer solution in Example 6.5.2 contained 0.135 M $\mathrm{HCO_2H}$ and 0.215 M $\mathrm{HCO_2Na}$ and had a pH of 3.95.

a. What is the final pH if 5.00 mL of 1.00 M HCl are added to 100 mL of this solution?
b. What is the final pH if 5.00 mL of 1.00 M $NaOH$ are added?

Given: composition and pH of buffer; concentration and volume of added acid or base

Asked for: final pH

Strategy:

A. Calculate the amounts of formic acid and formate present in the buffer solution using the procedure from Example 6.5.1 . Then calculate the amount of acid or base added.
B. Construct a table showing the amounts of all species after the neutralization reaction. Use the final volume of the solution to calculate the concentrations of all species. Finally, substitute the appropriate values into the Henderson-Hasselbalch approximation (Equation 5.2.1132) to obtain the pH.

Solution:

The added HCl (a strong acid) or NaOH (a strong base) will react completely with formate (a weak base) or formic acid (a weak acid), respectively, to give formic acid or formate and water. We must therefore calculate the amounts of formic acid and formate present after the neutralization reaction.

A We begin by calculating the millimoles of formic acid and formate present in 100 mL of the initial pH 3.95 buffer:

$$100\ \cancel{mL}\left(\frac{0.135\,mmol\ \mathrm{HCO_2H}}{\cancel{mL}}\right) = 13.5\,mmol\,\mathrm{HCO_2H}$$

$$100\ \cancel{mL}\left(\frac{0.215\,mmol\ \mathrm{HCO_2}^-}{\cancel{mL}}\right) = 21.5\,mmol\ {}_2\mathrm{HCO}^-$$

The millimoles of H^+ in 5.00 mL of 1.00 M HCl is as follows:

$$5.00\ \cancel{mL}\left(\frac{1.00\,mmol\ \mathrm{H}^+}{\cancel{mL}}\right) = 5\,mmol\,\mathrm{H}^+$$

B Next, we construct a table of initial amounts, changes in amounts, and final amounts:

$$\mathrm{HCO}^{2-}(\mathrm{aq}) + \mathrm{H}^+(\mathrm{aq}) \rightleftharpoons \mathrm{HCO_2H}(\mathrm{aq})$$

initial amounts, changes in amounts, and final amounts:

	$HCO^{2-}(aq)$	$H^+(aq)$	$HCO_2H(aq)$
Initial	21.5 mmol	5.00 mmol	13.5 mmol
Change	–5.00 mmol	–5.00 mmol	+5.00 mmol
Final	16.5 mmol	~0 mmol	18.5 mmol

The final amount of H^+ in solution is given as "~0 mmol." For the purposes of the stoichiometry calculation, this is essentially true, but remember that the point of the problem is to calculate the final $[H^+]$ and thus the pH. We now have all the information we need to calculate the pH. We can use either the lengthy procedure of Example 6.5.1 or the Henderson–Hasselbach approximation. Because we have performed many equilibrium calculations in this chapter, we'll take the latter approach. The Henderson-Hasselbalch approximation requires the concentrations of HCO_2^- and HCO_2H, which can be calculated using the number of millimoles (n) of each and the total volume (VT). Substituting these values into the Henderson-Hasselbalch approximation (Equation 5.2.1132):

$$\begin{aligned} pH &= pK_a + \log\left(\frac{[HCO_2^-]}{[HCO_2H]}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}/V_f}{n_{HCO_2H}/V_f}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \end{aligned}$$

Because the total volume appears in both the numerator and denominator, it cancels. We therefore need to use only the ratio of the number of millimoles of the conjugate base to the number of millimoles of the weak acid. So

$$pH = pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right)$$
$$= 3.75 + \log\left(\frac{16.5\ mmol}{18.5\ mmol}\right)$$
$$= 3.75\ - 0.050 = 3.70$$

Once again, this result makes sense on two levels. First, the addition of HClhas decreased the pH from 3.95, as expected. Second, the ratio of HCO_2^- to HCO_2H is slightly less than 1, so the pH should be between the pK_a and pK_a – 1.

A The procedure for solving this part of the problem is exactly the same as that used in part (a). We have already calculated the numbers of millimoles of formic acid and formate in 100 mL of the initial pH 3.95 buffer: 13.5 mmol of HCO_2H and 21.5 mmol of HCO_2^-. The number of millimoles of OH^- in 5.00 mL of 1.00 M $NaOH$ is as follows:

B With this information, we can construct a table of initial amounts, changes in amounts, and final amounts.

$$\mathrm{HCO_2H\,(aq) + OH^-\,(aq) \rightleftharpoons HCO_2^-\,(aq) + H_2O\,(l)}$$

initial amounts, changes in amounts, and final amounts

	$HCO_2H(aq)$	OH^-	$HCO_2^-(aq)$
Initial	13.5 mmol	5.00 mmol	21.5 mmol
Change	–5.00 mmol	–5.00 mmol	+5.00 mmol
Final	8.5 mmol	~0 mmol	26.5 mmol

The final amount of OH^- in solution is not actually zero; this is only approximately true based on the stoichiometric calculation. We can calculate the final pH by inserting the numbers of millimoles of both HCO_2^- and HCO_2H into the simplified Henderson-Hasselbalch expression used in part (a) because the volume cancels:

$$pH = pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right)$$
$$= 3.75 + \log\left(\frac{26.5\ mmol}{8.5\ mmol}\right)$$
$$= 3.75 + 0.494 = 4.24$$

Once again, this result makes chemical sense: the pH has increased, as would be expected after adding a strong base, and the final pH is between the pK_a and pK_a + 1, as expected for a solution with a HCO_2^-/HCO_2H ratio between 1 and 10.

Exercise 6.5.3

The buffer solution from Example 6.5.2 contained 0.119 M pyridine and 0.234 M pyridine hydrochloride and had a pH of 4.94.

a. What is the final pH if 12.0 mL of 1.5 M NaOH are added to 250 mL of this solution?
b. What is the final pH if 12.0 mL of 1.5 M HCl are added?

Answer a

5.30

Answer b

4.42

Only the amounts (in moles or millimoles) of the acidic and basic components of the buffer are needed to use the Henderson-Hasselbalch approximation, not their concentrations.

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A Video Discussing the Change in pH with the Addition of a Strong Acid to a Buffer: The Change in pH with the Addition of a Strong Acid to a Buffer(opens in new window) [youtu.be]

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The Change in pH with the Addition of a Strong Base to a Buffer:

The Change in pH with the Addition of a Strong Base to a Buffer (opens in new window) [youtu.be]

The results obtained in Example $6.5.3$ and its corresponding exercise demonstrate how little the pH of a well-chosen buffer solution changes despite the addition of a significant quantity of strong acid or strong base. Suppose we had added the same amount of HCl or $NaOH$ solution to 100 mL of an unbuffered solution at pH 3.95 (corresponding to 1.1×10^{-4} M HCl). In this case, adding 5.00 mL of 1.00 M HCl would lower the final pH to 1.32 instead of 3.70, whereas adding 5.00 mL of 1.00 M $NaOH$ would raise the final pH to 12.68 rather than 4.24. (Try verifying these values by doing the calculations yourself.) Thus the presence of a buffer significantly increases the ability of a solution to maintain an almost constant pH.

The most effective buffers contain **equal** concentrations of an acid and its conjugate base.

A buffer that contains approximately equal amounts of a weak acid and its conjugate base in solution is equally effective at neutralizing either added base or added acid. This is shown in Figure $6.5.2$ for an acetic acid/sodium acetate buffer. Adding a given amount of strong acid shifts the system along the horizontal axis to the left, whereas adding the same amount of strong base shifts the system the same distance to the right. In either case, the change in the ratio of $CH_3CO_2^-$ to CH_3CO_2H from 1:1 reduces the buffer capacity of the solution.

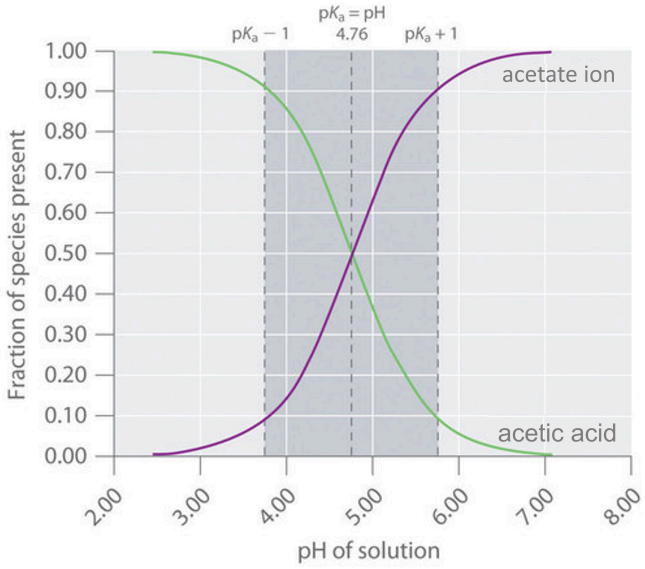


Figure 6.5.2: Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid. The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable concentrations of both species are present (pH 3.76–5.76, corresponding to $pH = pK_a \pm 1$). (CC BY-SA-NC; Anonymous by request)

Graph of mole fraction against pH of solution. The green line is acetic acid and the purple line is the acetate ion.

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A Video Discussing The Buffer Region: The Buffer Region (opens in new window) [youtu.be]

The Relationship between Titrations and Buffers

There is a strong correlation between the effectiveness of a buffer solution and the titration curves discussed in Section 16.5.

Consider the schematic titration curve of a weak acid with a strong base shown in Figure 6.5.3. As indicated by the labels, the region around pK_a corresponds to the midpoint of the titration, when approximately half the weak acid has been neutralized. This portion of the titration curve corresponds to a buffer: it exhibits the smallest change in pH per increment of added strong base, as shown by the nearly horizontal nature of the curve in this region. The nearly flat portion of the curve extends only from approximately a pH value of 1 unit less than the pK_a to approximately a pH value of 1 unit greater than the pK_a, which is why buffer solutions usually have a pH that is within ±1 pH units of the pK_a of the acid component of the buffer.

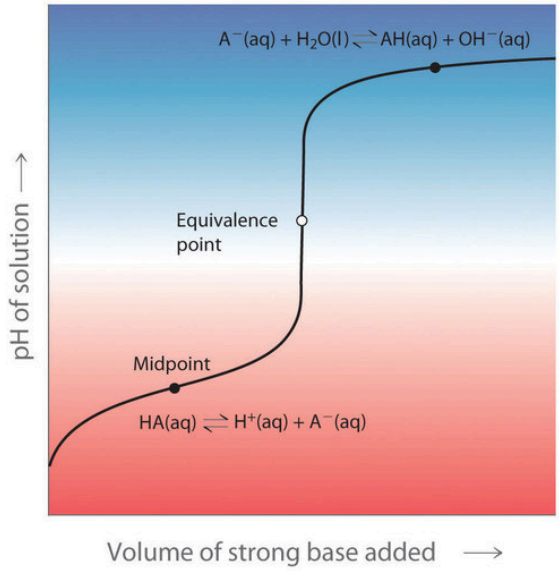


Figure 6.5.3: The Relationship between Titration Curves and Buffers. (CC BY-SA-NC; Anonymous by request)

Titration curves graph pH of solution against volume of strong base added. On the curve we look for the midpoints and equivalence points.

This schematic plot of pH for the titration of a weak acid with a strong base shows the nearly flat region of the titration curve around the midpoint, which corresponds to the formation of a buffer. At the lower left, the pH of the solution is determined by the equilibrium for dissociation of the weak acid; at the upper right, the pH is determined by the equilibrium for reaction of the conjugate base with water.

In the region of the titration curve at the lower left, before the midpoint, the acid–base properties of the solution are dominated by the equilibrium for dissociation of the weak acid, corresponding to K_a. In the region of the titration curve at the upper right, after the midpoint, the acid–base properties of the solution are dominated by the equilibrium for reaction of the conjugate base of the weak acid with water, corresponding to K_b. However, we can calculate either K_a or K_b from the other because they are related by K_w.

Blood: A Most Important Buffer

Metabolic processes produce large amounts of acids and bases, yet organisms are able to maintain an almost constant internal pH because their fluids contain buffers. This is not to say that the pH is uniform throughout all cells and tissues of a mammal. The internal pH of a red blood cell is about 7.2, but the pH of most other kinds of cells is lower, around 7.0. Even within a single cell, different compartments can have very different pH values. For example, one intracellular compartment in white blood cells has a pH of around 5.0.

Because no single buffer system can effectively maintain a constant pH value over the entire physiological range of approximately pH 5.0 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

The acid–base equilibrium in the CO_2/HCO_3^- buffer system is usually written as follows:

[redacted]

with $K_a = 4.5 \times 10^{-7}$ and $pK_a = 6.35$ at 25°C. In fact, Equation 5.2.1134 is a grossly oversimplified version of the CO_2/HCO_3^- system because a solution of CO_2 in water contains only rather small amounts of H_2CO_3. Thus Equation 5.2.1134 does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C.

As shown in Equation 5.2.1135, CO_2 is in equilibrium with H_2CO_3, but the equilibrium lies far to the left, with an H_2CO_3/CO_2 ratio less than 0.01 under most conditions:

[redacted]

with $K' = 4.0 \times 10^{-3}$ at 37°C. The true pK_a of carbonic acid at 37°C is therefore 3.70, not 6.35, corresponding to a K_a of 2.0×10^{-4}, which makes it a much stronger acid than Equation 5.2.1134 suggests. Adding Equation 5.2.1134 and Equation 5.2.1135 and canceling H_2CO_3 from both sides give the following overall equation for the reaction of CO_2 with water to give a proton and the bicarbonate ion:

[redacted]

with $K' = 4.0 \times 10^{-3} (37\ ^\circ C)$

[redacted]

with $K_a = 2.0 \times 10^{-4} (37\ ^\circ C)$

[redacted]

with $K = 8.0 \times 10^{-7} (37\ ^\circ C)$

The K value for the reaction in Equation 6.5.1251 is the product of the true ionization constant for carbonic acid (K_a) and the equilibrium constant (K) for the reaction of $CO_2\,(aq)$ with water to give carbonic acid. The equilibrium equation for the reaction of CO_2 with water to give bicarbonate and a proton is therefore

[redacted]

The presence of a gas in the equilibrium constant expression for a buffer is unusual. According to **Henry's law**,

$$[CO_2] = kP_{CO_2}$$

where k is the Henry's law constant for CO_2, which is $3.0 \times 10^{-5}\ \ M/mmHg$ at 37°C. Substituting this expression for $[CO_2]$ in Equation 1.6.891,

$$K = \frac{[H^+][HCO_3^-]}{(3.0 \times 10^{-5}\ M/mmHg)(P_{CO_2})}$$

where P_{CO_2} is in mmHg. Taking the negative logarithm of both sides and rearranging,

[redacted]

Thus the pH of the solution depends on both the CO_2 pressure over the solution and $[HCO_3^-]$. Figure 6.5.4 plots the relationship between pH and $[HCO_3^-]$ under physiological conditions for several different values of P_{CO_2}, with normal pH and $[HCO_3^-]$ values indicated by the dashed lines.

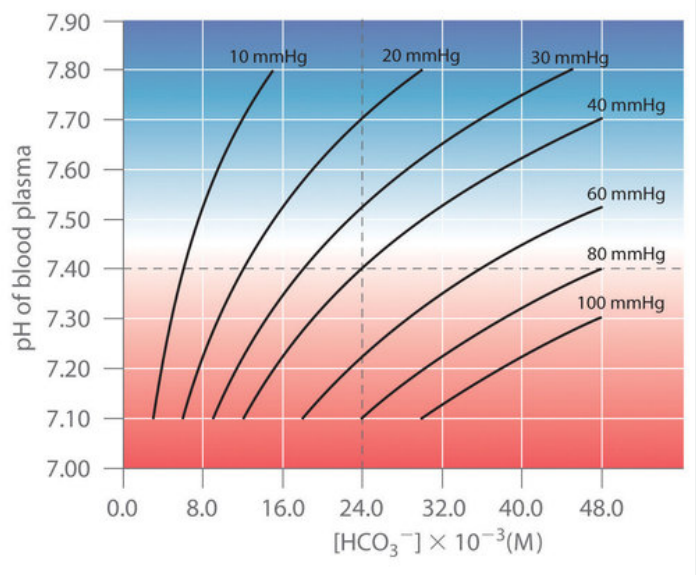


Figure 6.5.4: Buffering in Blood: pH versus $[\mathrm{HCO_3^-}]$ Curves for Buffers with Different Values of $P_{\mathrm{CO_2}}$. Only those combinations of pH and $[\mathrm{HCO_3^-}]$ that lie on a given line are allowed for the particular value of $P_{\mathrm{CO_2}}$ indicated. Normal values of blood plasma pH and $[\mathrm{HCO_3^-}]$ are indicated by dashed lines. (CC BY-SA-NC; Anonymous by request)

According to Equation 5.2.1141, adding a strong acid to the $\mathrm{CO_2/HCO_3^-}$ system causes $[\mathrm{HCO_3^-}]$ to decrease as $\mathrm{HCO_3^-}$ is converted to $\mathrm{CO_2}$. Excess $\mathrm{CO_2}$ is released in the lungs and exhaled into the atmosphere, however, so there is essentially no change in $P_{\mathrm{CO_2}}$. Because the change in $[\mathrm{HCO_3^-}]/P_{CO_2}$ is small, Equation 5.2.1141 predicts that the change in pH will also be rather small. Conversely, if a strong base is added, the $\mathrm{OH^-}$ reacts with $\mathrm{CO_2}$ to form $\mathrm{HCO_3^-}$, but $\mathrm{CO_2}$ is replenished by the body, again limiting the change in both $[\mathrm{HCO_3^-}]/P_{\mathrm{CO_2}}$ and pH. The $\mathrm{CO_2/HCO_3^-}$ buffer system is an example of an open system, in which the total concentration of the components of the buffer change to keep the pH at a nearly constant value.

If a passenger steps out of an airplane in Denver, Colorado, for example, the lower $P_{\mathrm{CO_2}}$ at higher elevations (typically 31 mmHg at an elevation of 2000 m versus 40 mmHg at sea level) causes a shift to a new pH and $[\mathrm{HCO_3^-}]$. The increase in pH and decrease in $[\mathrm{HCO_3^-}]$ in response to the decrease in $P_{\mathrm{CO_2}}$ are responsible for the general malaise that many people experience at high altitudes. If their blood pH does not adjust rapidly, the condition can develop into the life-threatening phenomenon known as altitude sickness.

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A Video Summary of the pH Curve for a Strong Acid/Strong Base Titration:

Summary of the pH Curve for a Strong Acid/Strong Base Titration(opens in new window) [youtu.be]

Summary

Buffers are solutions that resist a change in pH after adding an acid or a base. Buffers contain a weak acid (HA) and its conjugate weak base (A^-). Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium shifts the equilibrium in such a way as to reduce the concentration of the common ion. The shift in equilibrium is called the common ion effect. Buffers are characterized by their pH range and buffer capacity. The useful pH range of a buffer depends strongly on the chemical properties of the conjugate weak acid–base pair used to prepare the buffer (the K_a or K_b), whereas its buffer capacity depends solely on the concentrations of the species in the solution. The pH of a buffer can be calculated using the Henderson-Hasselbalch approximation, which is valid for solutions whose concentrations are at least 100 times greater than their K_a values. Because no single buffer system can effectively maintain a constant pH value over the physiological range of approximately 5 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

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6.6: Acid-Base Titration Curves

Learning Objectives

- To calculate the pH at any point in an acid–base titration.

In an acid–base titration, a buret is used to deliver measured volumes of an acid or a base solution of known concentration (the titrant) to a flask that contains a solution of a base or an acid, respectively, of unknown concentration (the unknown). If the concentration of the titrant is known, then the concentration of the unknown can be determined. The following discussion focuses on the pH changes that occur during an acid–base titration. Plotting the pH of the solution in the flask against the amount of acid or base added produces a titration curve. The shape of the curve provides important information about what is occurring in solution during the titration.

Titrations of Strong Acids and Bases

Figure $6.6.1a$ shows a plot of the pH as 0.20 M HCl is gradually added to 50.00 mL of pure water. The pH of the sample in the flask is initially 7.00 (as expected for pure water), but it drops very rapidly as HCl is added. Eventually the pH becomes constant at 0.70—a point well beyond its value of 1.00 with the addition of 50.0 mL of HCl (0.70 is the pH of 0.20 M HCl). In contrast, when 0.20 M NaOH is added to 50.00 mL of distilled water, the pH (initially 7.00) climbs very rapidly at first but then more gradually, eventually approaching a limit of 13.30 (the pH of 0.20 M NaOH), again well beyond its value of 13.00 with the addition of 50.0 mL of NaOH as shown in Figure $6.6.1b$. As you can see from these plots, the titration curve for adding a base is the mirror image of the curve for adding an acid.

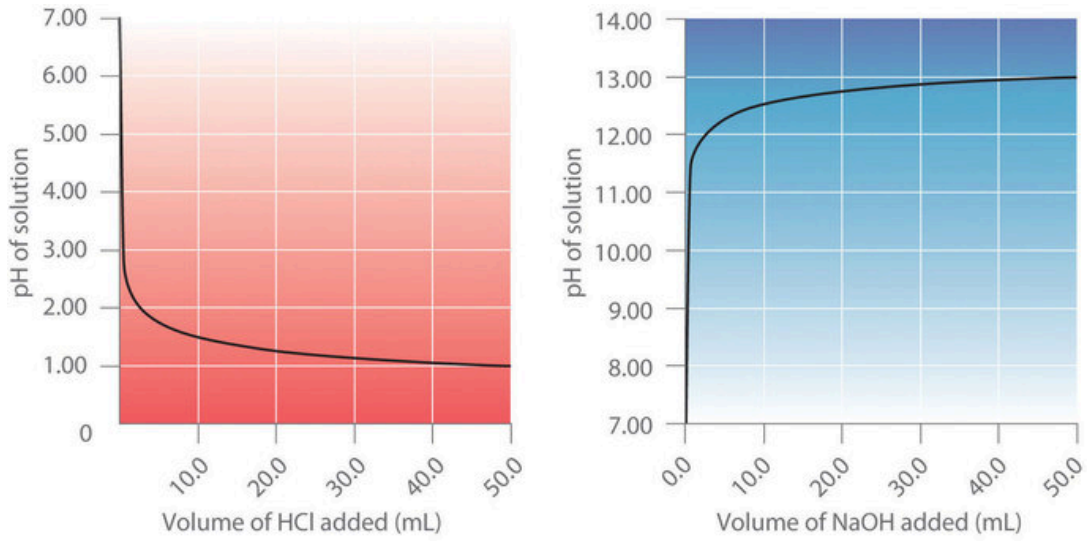


Figure $6.6.1$: Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water. (a) When 0.20 M HCl is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 M HCl. (b) Conversely, when 0.20 M NaOH is added to 50.0 mL of distilled water, the pH rapidly increases until it reaches a maximum at the pH of 0.20 M $NaOH$. (CC BY-SA-NC; Anonymous by request)

The graphs of water with strong acid added and water with strong base added are inverses of each other.

Suppose that we now add 0.20 M NaOH to 50.0 mL of a 0.10 M solution of HCl. Because HCl is a strong acid that is completely ionized in water, the initial $[H^+]$ is 0.10 M, and the initial pH is 1.00. Adding NaOH decreases the concentration of H+ because of the neutralization reaction (Figure $6.6.2a$):

$$\mathrm{OH^- + H^+ \rightleftharpoons H_2O}.$$

Thus the pH of the solution increases gradually. Near the equivalence point, however, the point at which the number of moles of base (or acid) added equals the number of moles of acid (or base) originally present in the solution, the pH increases much more rapidly because most of the H^+ ions originally present have been consumed. For the titration of a monoprotic strong acid (HCl) with a monobasic strong base ($NaOH$), we can calculate the volume of base needed to reach the equivalence point from the following relationship:

[redacted]

If 0.20 M $NaOH$ is added to 50.0 mL of a 0.10 M solution of HCl, we solve for V_b:

$$V_b(0.20Me) = 0.025L = 25mL$$

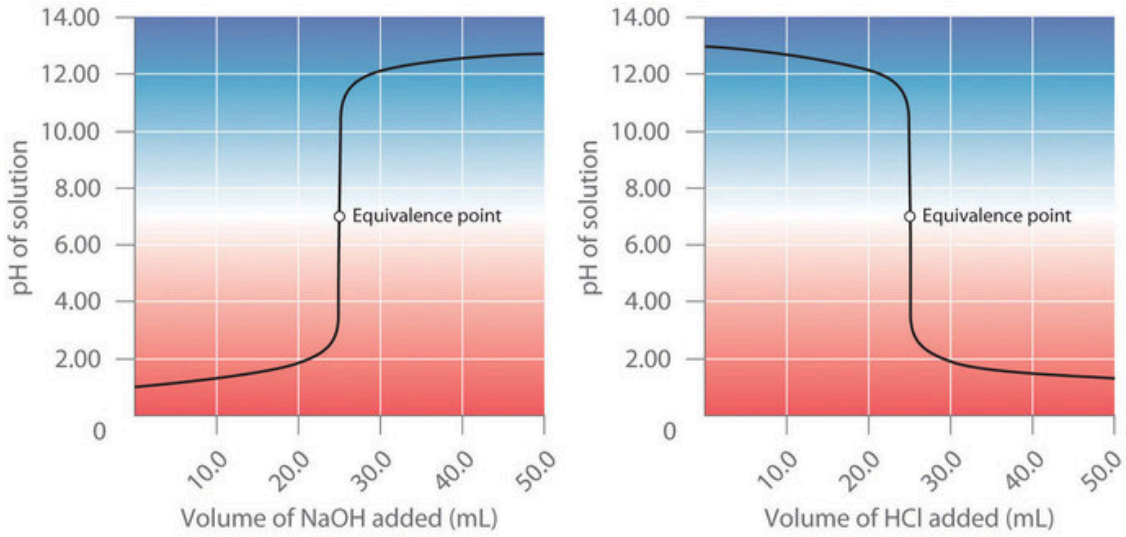


Figure 6.6.2: The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid(a) As 0.20 M $NaOH$ is slowly added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases slowly once more. (b) Conversely, as 0.20 M HCl is slowly added to 50.0 mL of 0.10 M $NaOH$, the pH decreases slowly at first, then decreases very rapidly as the equivalence point is approached, and finally decreases slowly once more. (CC BY-SA-NC; Anonymous by request)

The titration curves of strong acid titrated with strong base and strong base titrated with strong acid are inverses of each other.

At the equivalence point (when 25.0 mL of $NaOH$ solution has been added), the neutralization is complete: only a salt remains in solution (NaCl), and the pH of the solution is 7.00. Adding more $NaOH$ produces a rapid increase in pH, but eventually the pH levels off at a value of about 13.30, the pH of 0.20 M $NaOH$.

As shown in Figure 6.6.2b, the titration of 50.0 mL of a 0.10 M solution of $NaOH$ with 0.20 M HCl produces a titration curve that is nearly the mirror image of the titration curve in Figure 6.6.2a. The pH is initially 13.00, and it slowly decreases as HCl is added. As the equivalence point is approached, the pH drops rapidly before leveling off at a value of about 0.70, the pH of 0.20 M HCl.

The titration of either a strong acid with a strong base or a strong base with a strong acid produces an S-shaped curve. The curve is somewhat asymmetrical because the steady increase in the volume of the solution during the titration causes the solution to become more dilute. Due to the leveling effect, the shape of the curve for a titration involving a strong acid and a strong base depends on only the concentrations of the acid and base, not their identities.

> The shape of the titration curve involving a strong acid and a strong base depends only on their concentrations, not their identities.

Example 6.6.1: Hydrochloric Acid

Calculate the pH of the solution after 24.90 mL of 0.200 M $NaOH$ has been added to 50.00 mL of 0.100 M HCl.

Given: volumes and concentrations of strong base and acid

Asked for: pH

Strategy:

A. Calculate the number of millimoles of $\mathrm{H^+}$ and $\mathrm{OH^-}$ to determine which, if either, is in excess after the neutralization reaction has occurred. If one species is in excess, calculate the amount that remains after the neutralization reaction.
B. Determine the final volume of the solution. Calculate the concentration of the species in excess and convert this value to pH.

Solution

A Because 0.100 mol/L is equivalent to 0.100 mmol/mL, the number of millimoles of $\mathrm{H^+}$ in 50.00 mL of 0.100 M HCl can be calculated as follows:

$$50.00 \cancel{mL} \left(\frac{0.100\ mmol\ HCl}{\cancel{mL}} \right) = 5.00\ mmol\ HCl = 5.00\ mmol\ H^+$$

The number of millimoles of NaOH added is as follows:

$$24.90 \cancel{mL} \left(\frac{0.200\ mmol\ NaOH}{\cancel{mL}} \right) = 4.98\ mmol\ NaOH = 4.98\ mmol\ OH^-$$

Thus $\mathrm{H^+}$ is in excess. To completely neutralize the acid requires the addition of 5.00 mmol of $\mathrm{OH^-}$ to the HCl solution. Because only 4.98 mmol of OH^- has been added, the amount of excess $\mathrm{H^+}$ is 5.00 mmol – 4.98 mmol = 0.02 mmol of H^+.

B The final volume of the solution is 50.00 mL + 24.90 mL = 74.90 mL, so the final concentration of $\mathrm{H^+}$ is as follows:

$$[H^+] = \frac{0.02\ mmol\ H^+}{74.90\ mL} = 3 \times 10^{-4}\ M$$

Hence,

$$pH \approx -\log[\mathrm{H^+}] = -\log(3 \times 10^{-4}) = 3.5$$

This is significantly less than the pH of 7.00 for a neutral solution.

Exercise 6.6.1

Calculate the pH of a solution prepared by adding $40.00\ mL$ of $0.237\ M\ HCl$ to $75.00\ mL$ of a $0.133M$ solution of $NaOH$.

Answer

11.6

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pH after the addition of 10 ml of Strong Base to a Strong Acid:

https://youtu.be/_cM1_-kdJ20 (opens in new window)

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pH at the Equivalence Point in a Strong Acid/Strong Base Titration:

https://youtu.be/7POGDA5Ql2M

Titrations of Weak Acids and Bases

In contrast to strong acids and bases, the shape of the titration curve for a weak acid or a weak base depends dramatically on the identity of the acid or the base and the corresponding K_a or K_b. As we shall see, the pH also changes much more gradually around the equivalence point in the titration of a weak acid or a weak base. As you learned previously, $[\mathrm{H^+}]$ of a solution of a weak acid (HA) is not equal to the concentration of the acid but depends on both its pK_a and its concentration. Because only a fraction of a weak acid dissociates, [\($\mathrm{H^+}$] is less than $[\mathrm{HA}]$. Thus the pH of a solution of a weak acid is greater than the pH of a solution of a strong acid of the same concentration.

Figure $6.6.3a$ shows the titration curve for 50.0 mL of a 0.100 M solution of acetic acid with 0.200 M NaOH superimposed on the curve for the titration of 0.100 M HCl shown in part (a) in Figure $6.6.2$. Below the equivalence point, the two curves are very different. Before any base is added, the pH of the acetic acid solution is greater than the pH of the HCl solution, and the pH changes more rapidly during the first part of the titration. Note also that the pH of the acetic acid solution at the equivalence point is greater than 7.00. That is, at the equivalence point, the solution is basic. In addition, the change in pH around the equivalence point is only about half as large as for the HCl titration; the magnitude of the pH change at the equivalence point depends on the pK_a of the acid being titrated. Above the equivalence point, however, the two curves are identical. Once the acid has been neutralized, the pH of the solution is controlled only by the amount of excess NaOH present, regardless of whether the acid is weak or strong.

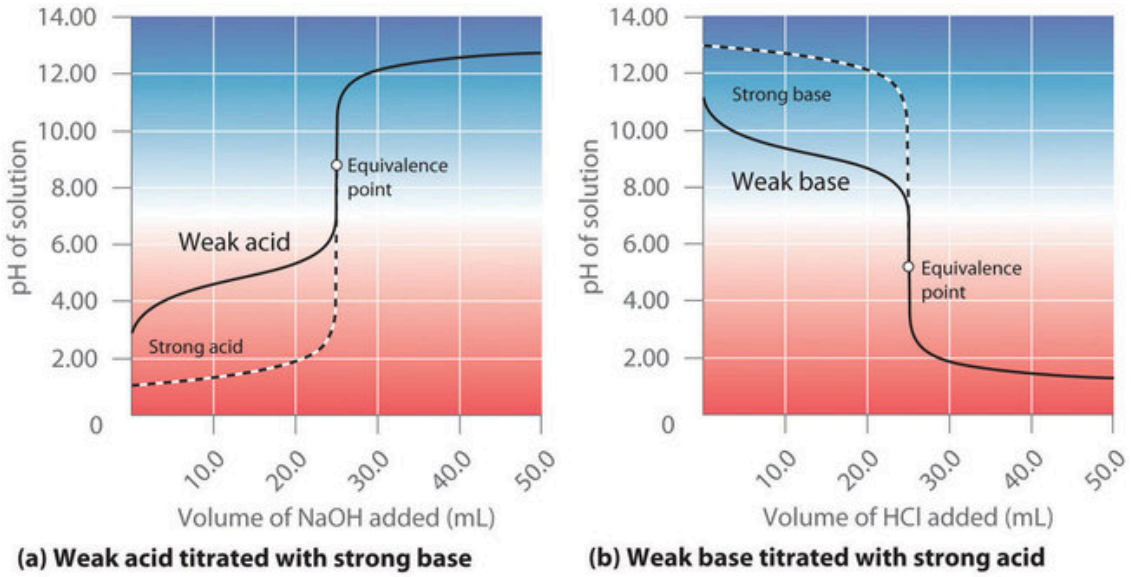


Figure 6.6.3: The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid. (a) As 0.200 M NaOH is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH is shown as a dashed line. (b) As 0.200 M HCl is slowly added to 50.0 mL of 0.100 M NH3, the pH decreases slowly at first, then decreases rapidly as the equivalence point is approached, and then again decreases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M NaOH with 0.200 M HCl is shown as a dashed line. (CC BY-SA-NC; Anonymous by request)

The titration curves of weak acid titrated with strong base and weak base titrated with strong acid are inverse of each other. These curves are shorter than the titration curves with strong acid and strong base.

> The shape of the titration curve of a weak acid or weak base depends heavily on their identities and the K_a or K_b.

The titration curve in Figure $6.6.3a$ was created by calculating the starting pH of the acetic acid solution before any NaOH is added and then calculating the pH of the solution after adding increasing volumes of $NaOH$. The procedure is illustrated in the following subsection and Example $6.6.2$ for three points on the titration curve, using the pK_a of acetic acid (4.76 at 25°C; $K_a = 1.7 \times 10^{-5}$.

Calculating the pH of a Solution of a Weak Acid or a Weak Base

As explained discussed, if we know K_a or K_b and the initial concentration of a weak acid or a weak base, we can calculate the pH of a solution of a weak acid or a weak base by setting up a ICE table (i.e, initial concentrations, changes in concentrations, and final concentrations). In this situation, the initial concentration of acetic acid is 0.100 M. If we define x as $[\mathrm{H}^+]$ due to the dissociation of the acid, then the table of concentrations for the ionization of 0.100 M acetic acid is as follows:

$$\mathrm{CH_3CO_2H\,(aq) \rightleftharpoons H^+\,(aq) + CH_3CO_2{}^-}$$

table of concentrations for the ionization of 0.100 M acetic acid

ICE	$[CH_3CO_2H]$	$[H^+]$	$[CH_3CO_2^-]$
initial	0.100	1.00×10^{-7}	0
change	–x	+x	+x
final	0.100 – x	x	x

In this and all subsequent examples, we will ignore $[H^+]$ and $[OH^-]$ due to the autoionization of water when calculating the final concentration. However, you should use Equation 16.45 and Equation 16.46 to check that this assumption is justified.

Inserting the expressions for the final concentrations into the equilibrium equation (and using approximations),

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$
$$= \frac{(x)(x)}{0.100 - x}$$
$$\approx \frac{x^2}{0.100}$$
$$\approx 1.74 \times 10^{-5}$$

Solving this equation gives $x = [H^+] = 1.32 \times 10^{-3}\ M$. Thus the pH of a 0.100 M solution of acetic acid is as follows:

$$pH = -\log(1.32 \times 10^{-3}) = 2.879$$

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https://www.youtube.com/embed/AtdBKfrfJNg?vq=hd1080

pH at the Start of a Weak Acid/Strong Base Titration: https://youtu.be/AtdBKfrfJNg

Calculating the pH during the Titration of a Weak Acid or a Weak Base

Now consider what happens when we add 5.00 mL of 0.200 M NaOH to 50.00 mL of 0.100 M CH_3CO_2H (part (a) in Figure 6.6.3). Because the neutralization reaction proceeds to completion, all of the OH^- ions added will react with the acetic acid to generate acetate ion and water:

[redacted]

All problems of this type must be solved in two steps: a stoichiometric calculation followed by an equilibrium calculation. In the first step, we use the stoichiometry of the neutralization reaction to calculate the amounts of acid and conjugate base present in solution after the neutralization reaction has occurred. In the second step, we use the equilibrium equation to determine $[\mathrm{H}^+]$ of the resulting solution.

Step 1

To determine the amount of acid and conjugate base in solution after the neutralization reaction, we calculate the amount of

CH_3CO_2H in the original solution and the amount of OH^- in the $NaOH$ solution that was added. The acetic acid solution contained

$$50.00\ \cancel{mL}\ (0.100\ mmol(CH_3CO_2H)/\cancel{mL}) = 5.00\ mmol(CH_3CO_2H)$$

The $NaOH$ solution contained

5.00 mL=1.00 mmol $NaOH$

Comparing the amounts shows that CH_3CO_2H is in excess. Because OH^- reacts with CH_3CO_2H in a 1:1 stoichiometry, the amount of excess CH_3CO_2H is as follows:

5.00 mmol CH_3CO_2H – 1.00 mmol OH^- = 4.00 mmol CH_3CO_2H

Each 1 mmol of OH^- reacts to produce 1 mmol of acetate ion, so the final amount of $CH_3CO_2^-$ is 1.00 mmol.

The stoichiometry of the reaction is summarized in the following ICE table, which shows the numbers of moles of the various species, not their concentrations.

$$CH_3CO_2H\,(aq) + OH^-\,(aq) \rightleftharpoons CH_3CO_2{}^-\,(aq) + H_2O\,(l)$$

ICE table

ICE	$[CH_3CO_2H]$	$[OH^-]$	$[CH_3CO_2^-]$
initial	5.00 mmol	1.00 mmol	0 mmol
change	–1.00 mmol	–1.00 mmol	+1.00 mmol
final	4.00 mmol	0 mmol	1.00 mmol

This ICE table gives the initial amount of acetate and the final amount of OH^- ions as 0. Because an aqueous solution of acetic acid always contains at least a small amount of acetate ion in equilibrium with acetic acid, however, the initial acetate concentration is not actually 0. The value can be ignored in this calculation because the amount of $CH_3CO_2^-$ in equilibrium is insignificant compared to the amount of OH^- added. Moreover, due to the autoionization of water, no aqueous solution can contain 0 mmol of OH^-, but the amount of OH^- due to the autoionization of water is insignificant compared to the amount of OH^- added. We use the initial amounts of the reactants to determine the stoichiometry of the reaction and defer a consideration of the equilibrium until the second half of the problem.

Step 2

To calculate $[H^+]$ at equilibrium following the addition of $NaOH$, we must first calculate $[CH_3CO_2H]$ and $[CH_3CO_2{}^-]$ using the number of millimoles of each and the total volume of the solution at this point in the titration:

$$final\ volume = 50.00\ mL + 5.00\ mL = 55.00\ mL$$

$$[CH_3CO_2H] = \frac{4.00\ mmol\ CH_3CO_2H}{55.00\ mL} = 7.27 \times 10^{-2}\ M$$

$$[CH_3CO_2^-] = \frac{1.00\ mmol\ CH_3CO_2^-}{55.00\ mL} = 1.82 \times 10^{-2}\ M$$

Knowing the concentrations of acetic acid and acetate ion at equilibrium and K_a for acetic acid (1.74×10^{-5}), we can calculate $[H^+]$ at equilibrium:

$$K_a = \frac{[CH_3CO_2^-]\,[H^+]}{[CH_3CO_2H]}$$

$$[H^+] = \frac{K_a\,[CH_3CO_2H]}{[CH_3CO_2^-]} = \frac{(1.72 \times 10^{-5})\,(7.27 \times 10^{-2}\ M)}{(1.82 \times 10^{-2})} = 6.95 \times 10^{-5}\ M$$

Calculating $-\log[H^+]$ gives

$$pH = -\log(6.95 \times 10^{-5}) = 4.158.$$

Comparing the titration curves for HCl and acetic acid in Figure $6.6.3a$, we see that adding the same amount (5.00 mL) of 0.200 M NaOH to 50 mL of a 0.100 M solution of both acids causes a much smaller pH change for HCl (from 1.00 to 1.14) than for acetic acid (2.88 to 4.16). This is consistent with the qualitative description of the shapes of the titration curves at the beginning of this section. In Example $6.6.2$, we calculate another point for constructing the titration curve of acetic acid.

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https://www.youtube.com/embed/znpwGCsefXc?vq=hd1080

pH Before the Equivalence Point of a Weak Acid/Strong Base Titration:

https://youtu.be/znpwGCsefXc

Example $6.6.2$

What is the pH of the solution after 25.00 mL of 0.200 M NaOH is added to 50.00 mL of 0.100 M acetic acid?

Given: volume and molarity of base and acid

Asked for: pH

Strategy:

A. Write the balanced chemical equation for the reaction. Then calculate the initial numbers of millimoles of OH^- and CH_3CO_2H. Determine which species, if either, is present in excess.
B. Tabulate the results showing initial numbers, changes, and final numbers of millimoles.
C. If excess acetate is present after the reaction with OH^-, write the equation for the reaction of acetate with water. Use a tabular format to obtain the concentrations of all the species present.
D. Calculate K_b using the relationship $K_w = K_aK_b$. Calculate [OH–] and use this to calculate the pH of the solution.

Solution

A Ignoring the spectator ion (Na^+), the equation for this reaction is as follows:

$$CH_3CO_2H_{(aq)} + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l)$$

The initial numbers of millimoles of OH^- and CH_3CO_2H are as follows:

25.00 mL(0.200 mmol OH–mL=5.00 mmol $OH-$

$$50.00\ mL(0.100 CH_3CO_2HL = 5.00 mmol\ CH_3CO_2H$$

The number of millimoles of OH^- equals the number of millimoles of CH_3CO_2H, so neither species is present in excess.

B Because the number of millimoles of OH^- added corresponds to the number of millimoles of acetic acid in solution, this is the equivalence point. The results of the neutralization reaction can be summarized in tabular form.

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3CO_2^-(aq) + H_2O(l)$$

results of the neutralization reaction

ICE	$[CH_3CO_2H]$	$[OH^-]$	$[CH_3CO_2^-]$
initial	5.00 mmol	5.00 mmol	0 mmol
change	–5.00 mmol	–5.00 mmol	+5.00 mmol
final	0 mmol	0 mmol	5.00 mmol

C Because the product of the neutralization reaction is a weak base, we must consider the reaction of the weak base with water to calculate [H+] at equilibrium and thus the final pH of the solution. The initial concentration of acetate is obtained from the neutralization reaction:

$$[\mathrm{CH_3CO_2}] = \frac{5.00\ mmol\ CH_3CO_2^-}{(50.00 + 25.00)\ mL} = 6.67 \times 10^{-2}\ M$$

The equilibrium reaction of acetate with water is as follows:

$$\mathrm{CH_3CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3CO_2H\,(aq) + OH^-\,(aq)}$$

The equilibrium constant for this reaction is

[redacted]

where K_a is the acid ionization constant of acetic acid. We therefore define x as $[\mathrm{OH^-}]$ produced by the reaction of acetate with water. Here is the completed table of concentrations:

$$H_2O_{(l)} + CH_3CO_{2(aq)}^- \rightleftharpoons CH_3CO_2H_{(aq)} + OH^-_{(aq)}$$

completed table of concentrations

	$[CH_3CO_2^-]$	$[CH_3CO_2H]$	$[OH^-]$
initial	0.0667	0	1.00 × 10–7
change	–x	+x	+x
final	(0.0667 – x)	x	x

D We can obtain K_b by substituting the known values into Equation 6.6.1252:

[redacted]

Substituting the expressions for the final values from the ICE table into Equation 6.6.1253 and solving for x:

$$\frac{x^2}{0.0667} = 5.80 \times 10^{-10}$$

$$x = \sqrt{(5.80 \times 10^{-10})(0.0667)}$$

$$= 6.22 \times 10^{-6}$$

Thus $[OH^-] = 6.22 \times 10^{-6}\ M$ and the pH of the final solution is 8.794 (Figure $6.6.3a$). As expected for the titration of a weak acid, the pH at the equivalence point is greater than 7.00 because the product of the titration is a base, the acetate ion, which then reacts with water to produce $\mathrm{OH^-}$.

Exercise 6.6.2

Calculate the pH of a solution prepared by adding 45.0 mL of a 0.213 M HCl solution to 125.0 mL of a 0.150 M solution of ammonia. The pK_b of ammonia is 4.75 at 25°C.

Answer

9.23

As shown in part (b) in Figure 6.6.3, the titration curve for NH3, a weak base, is the reverse of the titration curve for acetic acid. In particular, the pH at the equivalence point in the titration of a weak base is less than 7.00 because the titration produces an acid.

The identity of the weak acid or weak base being titrated strongly affects the shape of the titration curve. Figure 6.6.4 illustrates the shape of titration curves as a function of the pK_a or the pK_b. As the acid or the base being titrated becomes weaker (its pK_a or pK_b becomes larger), the pH change around the equivalence point decreases significantly. With very dilute solutions, the curve becomes so shallow that it can no longer be used to determine the equivalence point.

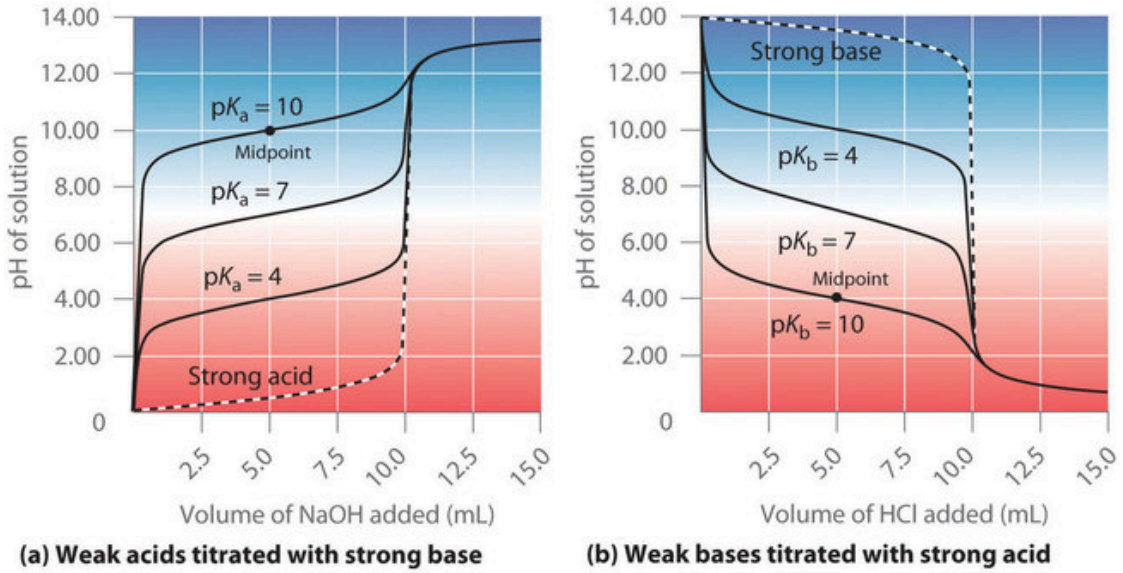


Figure 6.6.4: Effect of Acid or Base Strength on the Shape of Titration Curves. Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the pK_a or pK_b of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M NaOH added to 10.00 mL of 1.00 M solutions of weak acids with the indicated pK_a values. (b) Solution pH as a function of the volume of 1.00 M HCl added to 10.00 mL of 1.00 M solutions of weak bases with the indicated pK_b values. The shapes of the two sets of curves are essentially identical, but one is flipped vertically in relation to the other. Midpoints are indicated for the titration curves corresponding to pK_a = 10 and pK_b = 10. (CC BY-SA-NC; Anonymous by request)

The titration curves of weak acids with strong base and weak bases titrated with strong acid are inverses of each other. Three weak acids and three weak bases with pKa and pKb of 4, 7, and 10 are used.

One point in the titration of a weak acid or a weak base is particularly important: the midpoint of a titration is defined as the point at which exactly enough acid (or base) has been added to neutralize one-half of the acid (or the base) originally present and occurs halfway to the equivalence point. The midpoint is indicated in Figures $6.6.4a$ and $6.6.4b$ for the two shallowest curves. By definition, at the midpoint of the titration of an acid, [HA] = [A–]. Recall that the ionization constant for a weak acid is as follows:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

If $[HA] = [A^-]$, this reduces to $K_a = [H_3O^+]$. Taking the negative logarithm of both sides,

$$-\log K_a = -\log[H_3O+]$$

From the definitions of pK_a and pH, we see that this is identical to

[redacted]

Thus the pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid, as indicated in part (a) in Figure $6.6.4$ for the weakest acid where we see that the midpoint for pK_a = 10 occurs at pH = 10. Titration methods can therefore be used to determine both the concentration and the pK_a (or the pK_b) of a weak acid (or a weak base).

> The pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid.

Titrations of Polyprotic Acids or Bases

When a strong base is added to a solution of a polyprotic acid, the neutralization reaction occurs in stages. The most acidic group is titrated first, followed by the next most acidic, and so forth. If the pK_a values are separated by at least three pK_a units, then the overall titration curve shows well-resolved “steps” corresponding to the titration of each proton. A titration of the triprotic acid H_3PO_4 with NaOH is illustrated in Figure $6.6.5$ and shows two well-defined steps: the first midpoint corresponds to pK_a1, and the second midpoint corresponds to pK_a2. Because HPO_4^{2-} is such a weak acid, pK_a3 has such a high value that the third step cannot be resolved using 0.100 M NaOH as the titrant.

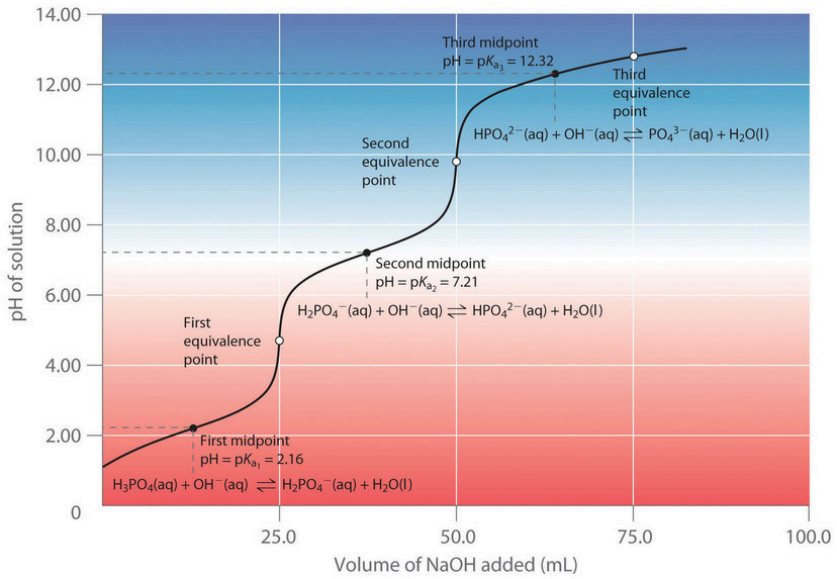
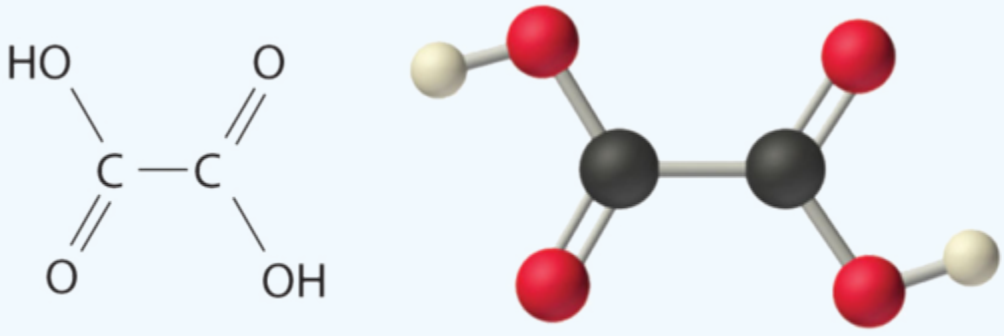


Figure 6.6.5: Titration Curve for Phosphoric Acid (H_3PO_4, a Typical Polyprotic Acid. The curve for the titration of 25.0 mL of a 0.100 M H_3PO_4 solution with 0.100 M NaOH along with the species in solution at each Ka is shown. Note the two distinct equivalence points corresponding to deprotonation of H_3PO_4 at pH ≈ 4.6 and $H_2PO_4^{2-}$ at pH ≈ 9.8. Because HPO_4^{2-} is a very weak acid, the third equivalence point, at pH ≈ 13, is not well defined. (CC BY-SA-NC; Anonymous by request)

The titration curve for the reaction of a polyprotic base with a strong acid is the mirror image of the curve shown in Figure 6.6.5 . The initial pH is high, but as acid is added, the pH decreases in steps if the successive pK_b values are well separated. Table E1 lists the ionization constants and pK_a values for some common polyprotic acids and bases.

Example 6.6.3

Calculate the pH of a solution prepared by adding 55.0 mL of a 0.120 M NaOH solution to 100.0 mL of a 0.0510 M solution of oxalic acid ($\mathrm{HO_2CCO_2H}$), a diprotic acid (abbreviated as $\mathrm{H_2ox}$). Oxalic acid, the simplest dicarboxylic acid, is found in rhubarb and many other plants. Rhubarb leaves are toxic because they contain the calcium salt of the fully deprotonated form of oxalic acid, the oxalate ion ($\mathrm{O_2CCO_2}^{2-}$, abbreviated ox^{2-}).Oxalate salts are toxic for two reasons. First, oxalate salts of divalent cations such as Ca^{2+} are insoluble at neutral pH but soluble at low pH. As a result, calcium oxalate dissolves in the dilute acid of the stomach, allowing oxalate to be absorbed and transported into cells, where it can react with calcium to form tiny calcium oxalate crystals that damage tissues. Second, oxalate forms stable complexes with metal ions, which can alter the distribution of metal ions in biological fluids.



oxalic acid

Given: volume and concentration of acid and base

Asked for: pH

Strategy:

A. Calculate the initial millimoles of the acid and the base. Use a tabular format to determine the amounts of all the species in solution.
B. Calculate the concentrations of all the species in the final solution. Determine $[H+]$ and convert this value to pH.

Solution:

A Table E5 gives the pK_a values of oxalic acid as 1.25 and 3.81. Again we proceed by determining the millimoles of acid and base initially present:

$$100.00 \cancel{mL} \left(\frac{0.510\ mmol\ H_2ox}{\cancel{mL}} \right) = 5.10\ mmol\ H_2ox$$

$$55.00 \cancel{mL} \left(\frac{0.120\ mmol\ NaOH}{\cancel{mL}} \right) = 6.60\ mmol\ NaOH$$

The strongest acid (H_2ox) reacts with the base first. This leaves (6.60 – 5.10) = 1.50 mmol of OH^- to react with Hox–, forming ox^{2-} and H_2O. The reactions can be written as follows:

$$\underset{5.10\ mmol}{H_2ox} + \underset{6.60\ mmol}{OH^-} \rightarrow \underset{5.10\ mmol}{Hox^-} + \underset{5.10\ mmol}{H_2O}$$

$$\underset{5.10\ mmol}{Hox^-} + \underset{1.50\ mmol}{OH^-} \rightarrow \underset{1.50\ mmol}{ox^{2-}} + \underset{1.50\ mmol}{H_2O}$$

In tabular form,

Solutions to Example 17.3.3

	H_2ox	OH^-	Hox^-	ox^{2-}
initial	5.10 mmol	6.60 mmol	0 mmol	0 mmol
change (step 1)	–5.10 mmol	–5.10 mmol	+5.10 mmol	0 mmol
final (step 1)	0 mmol	1.50 mmol	5.10 mmol	0 mmol
change (step 2)	—	–1.50 mmol	–1.50 mmol	+1.50 mmol
final	0 mmol	0 mmol	3.60 mmol	1.50 mmol

B The equilibrium between the weak acid (Hox^-) and its conjugate base (ox^{2-}) in the final solution is determined by the magnitude of the second ionization constant, $K_{a2} = 10^{-3.81} = 1.6 \times 10^{-4}$. To calculate the pH of the solution, we need to know $[H^+]$, which is determined using exactly the same method as in the acetic acid titration in Example 6.6.2:

$$\text{final volume of solution} = 100.0\,mL + 55.0\,mL = 155.0\,mL$$

Thus the concentrations of Hox^- and ox^{2-} are as follows:

$$[Hox^-] = \frac{3.60\ mmol\ Hox^-}{155.0\ mL} = 2.32 \times 10^{-2}\ M$$

$$[ox^{2-}] = \frac{1.50\ mmol\ ox^{2-}}{155.0\ mL} = 9.68 \times 10^{-3}\ M$$

We can now calculate [H+] at equilibrium using the following equation:

$$K_{a2} = \frac{[ox^{2-}]\,[H^+]}{[Hox^-]}$$

Rearranging this equation and substituting the values for the concentrations of Hox^- and ox^{2-},

$$[H^+] = \frac{K_{a2}\,[Hox^-]}{[ox^{2-}]} = \frac{\left(1.6 \times 10^{-4}\right)\left(2.32 \times 10^{-2}\right)}{\left(9.68 \times 10^{-3}\right)} = 3.7 \times 10^{-4}\ M$$

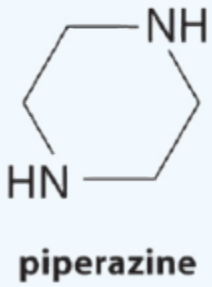
So

$$pH = -\log\left[H^+\right] = -\log\left(3.7 \times 10^{-4}\right) = 3.43$$

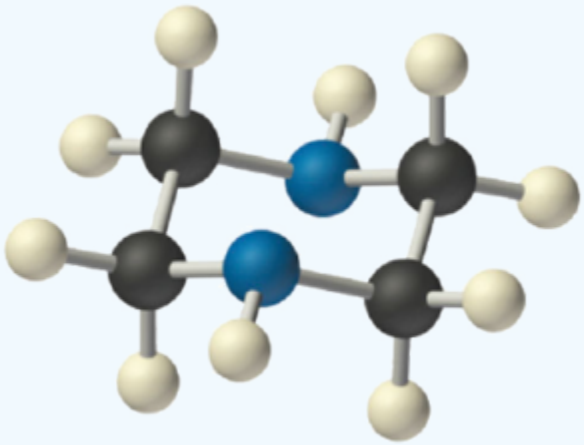
This answer makes chemical sense because the pH is between the first and second pK_a values of oxalic acid, as it must be. We added enough hydroxide ion to completely titrate the first, more acidic proton (which should give us a pH greater than pK_{a1}), but we added only enough to titrate less than half of the second, less acidic proton, with pK_{a2}. If we had added exactly enough hydroxide to completely titrate the first proton plus half of the second, we would be at the midpoint of the second step in the titration, and the pH would be 3.81, equal to pK_{a2}.

Exercise 6.6.3: Piperazine

Piperazine is a diprotic base used to control intestinal parasites (“worms”) in pets and humans. A dog is given 500 mg (5.80 mmol) of piperazine (pK_{b1} = 4.27, pK_{b2} = 8.67). If the dog’s stomach initially contains 100 mL of 0.10 M HCl (pH = 1.00), calculate the pH of the stomach contents after ingestion of the piperazine.



piperazine



Answer

pH=4.9

Indicators

In practice, most acid–base titrations are not monitored by recording the pH as a function of the amount of the strong acid or base solution used as the titrant. Instead, an acid–base indicator is often used that, if carefully selected, undergoes a dramatic color change at the pH corresponding to the equivalence point of the titration. Indicators are weak acids or bases that exhibit intense colors that vary with pH. The conjugate acid and conjugate base of a good indicator have very different colors so that they can be distinguished easily. Some indicators are colorless in the conjugate acid form but intensely colored when deprotonated

(phenolphthalein, for example), which makes them particularly useful.

We can describe the chemistry of indicators by the following general equation:

$$\mathrm{HIn\,(aq)} \rightleftharpoons \mathrm{H^+\,(aq)} + \mathrm{In^-\,(aq)}$$

where the protonated form is designated by HIn and the conjugate base by $\mathrm{In^-}$. The ionization constant for the deprotonation of indicator HIn is as follows:

[redacted]

The pK_{in} (its pK_a) determines the pH at which the indicator changes color.

Many different substances can be used as indicators, depending on the particular reaction to be monitored. For example, red cabbage juice contains a mixture of colored substances that change from deep red at low pH to light blue at intermediate pH to yellow at high pH. Similarly, *Hydrangea macrophylla* flowers can be blue, red, pink, light purple, or dark purple depending on the soil pH (Figure $6.6.6$). Acidic soils will produce blue flowers, whereas alkaline soils will produce pinkish flowers.

Irrespective of the origins, a good indicator must have the following properties:

- The color change must be easily detected.
- The color change must be rapid.
- The indicator molecule must not react with the substance being titrated.
- To minimize errors, the indicator should have a pK_{in} that is within one pH unit of the expected pH at the equivalence point of the titration.



Figure $6.6.6$: Naturally occurring pH indicators can be found in red cabbage and Hydrangea macrophylla flowers. Red Cabbage image (CC BY-SA 3.0; KENPEI via Wikipedia) and Hydrangea macrophylla flowers (pixabay).

Synthetic indicators have been developed that meet these criteria and cover virtually the entire pH range. Figure $6.6.7$ shows the approximate pH range over which some common indicators change color and their change in color. In addition, some indicators (such as thymol blue) are polyprotic acids or bases, which change color twice at widely separated pH values.

Indicator	pK_{in}	Color change
Alizarin yellow R	11.0	yellow to red
Thymolphthalein	9.9	colorless to blue
Phenolphthalein	9.5	colorless to pink
Thymol blue	9.2	yellow to blue
Phenol red	7.4	yellow to red
Bromothymol blue	7.3	yellow to blue
Bromocresol purple	6.4	yellow to purple
Ethyl red	5.4	colorless to red
Resorcin blue	5.3	red to blue
Resazurin	5.1	orange to violet
Methyl red	5.0	red to yellow
Bromophenol blue	4.1	yellow to blue
Thymol blue	1.7	red to yellow
Malachite green	1.3	yellow to turquoise
Methyl violet	0.8	yellow to blue

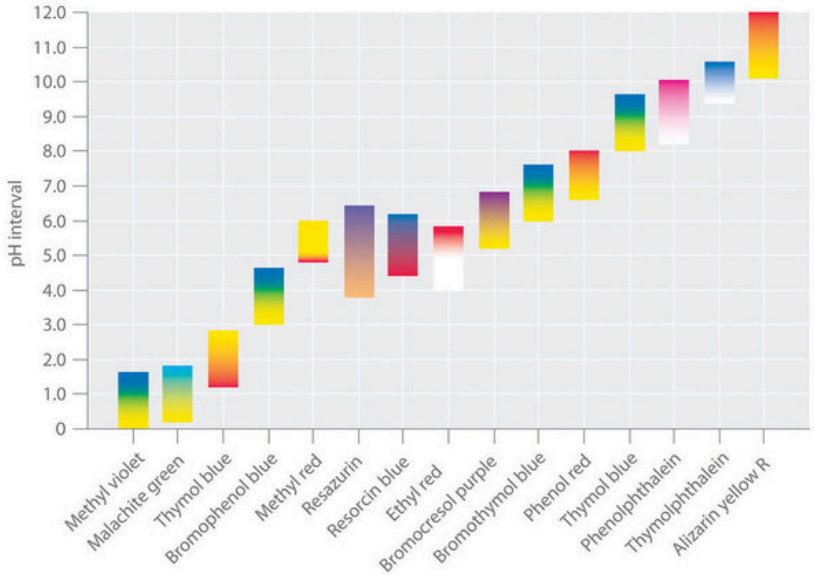


Figure 6.6.7: Some Common Acid–Base Indicators. Approximate colors are shown, along with pK_{in} values and the pH range over which the color changes. (CC BY-SA-NC; Anonymous by request)

It is important to be aware that an indicator does not change color abruptly at a particular pH value; instead, it actually undergoes a pH titration just like any other acid or base. As the concentration of HIn decreases and the concentration of In– increases, the color of the solution slowly changes from the characteristic color of HIn to that of In–. As we will see later, the [In–]/[HIn] ratio changes from 0.1 at a pH one unit below pKin to 10 at a pH one unit above pKin. Thus most indicators change color over a pH range of about two pH units.

We have stated that a good indicator should have a pKin value that is close to the expected pH at the equivalence point. For a strong acid–strong base titration, the choice of the indicator is not especially critical due to the very large change in pH that occurs around the equivalence point. In contrast, using the wrong indicator for a titration of a weak acid or a weak base can result in relatively large errors, as illustrated in Figure 6.6.8. This figure shows plots of pH versus volume of base added for the titration of 50.0 mL of a 0.100 M solution of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M $NaOH$. The pH ranges over which two common indicators (methyl red, $pK_{in} = 5.0$, and phenolphthalein, $pK_{in} = 9.5$) change color are also shown. The horizontal bars indicate the pH ranges over which both indicators change color cross the HCl titration curve, where it is almost vertical. Hence both indicators change color when essentially the same volume of NaOH has been added (about 50 mL), which corresponds to the equivalence point. In contrast, the titration of acetic acid will give very different results depending on whether methyl red or phenolphthalein is used as the indicator. Although the pH range over which phenolphthalein changes color is slightly greater than the pH at the equivalence point of the strong acid titration, the error will be negligible due to the slope of this portion of the titration curve. Just as with the HCl titration, the phenolphthalein indicator will turn pink when about 50 mL of NaOH has been added to the acetic acid solution. In contrast, methyl red begins to change from red to yellow around pH 5, which is near the midpoint of the acetic acid titration, not the equivalence point. Adding only about 25–30 mL of NaOH will therefore cause the methyl red indicator to change color, resulting in a huge error.

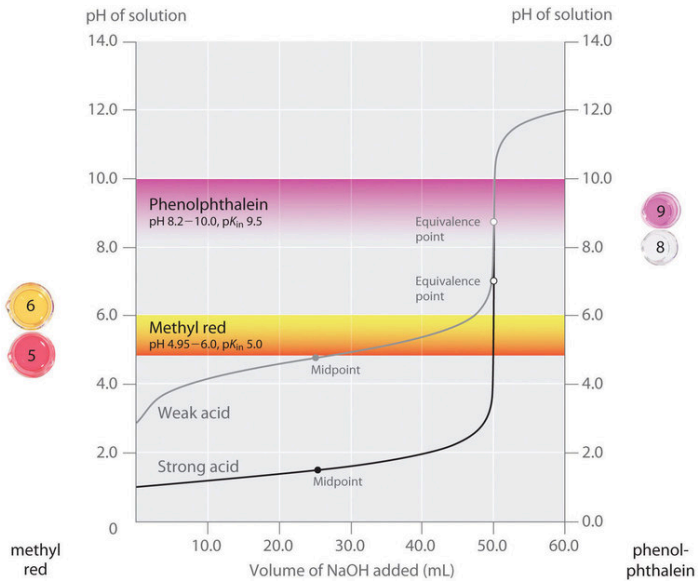


Figure 6.6.8: Choosing the Correct Indicator for an Acid–Base Titration. (CC BY-SA-NC; Anonymous by request)

If the pH of the solution is between 4.95 and 6 then methyl red should be used. If the pH is between 8,2 and 10 then phenolphthalein should be used.

The graph shows the results obtained using two indicators (methyl red and phenolphthalein) for the titration of 0.100 M solutions of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M $NaOH$. Due to the steepness of the titration curve of a strong acid around the equivalence point, either indicator will rapidly change color at the equivalence point for the titration of the strong acid. In contrast, the pKin for methyl red (5.0) is very close to the pK_a of acetic acid (4.76); the midpoint of the color change for methyl red occurs near the midpoint of the titration, rather than at the equivalence point.

In general, for titrations of strong acids with strong bases (and vice versa), any indicator with a pKin between about 4.0 and 10.0 will do. For the titration of a weak acid, however, the pH at the equivalence point is greater than 7.0, so an indicator such as phenolphthalein or thymol blue, with pKin > 7.0, should be used. Conversely, for the titration of a weak base, where the pH at the equivalence point is less than 7.0, an indicator such as methyl red or bromocresol blue, with pKin < 7.0, should be used.

The existence of many different indicators with different colors and pKin values also provides a convenient way to estimate the pH of a solution without using an expensive electronic pH meter and a fragile pH electrode. Paper or plastic strips impregnated with combinations of indicators are used as “pH paper,” which allows you to estimate the pH of a solution by simply dipping a piece of pH paper into it and comparing the resulting color with the standards printed on the container (Figure 6.6.9).

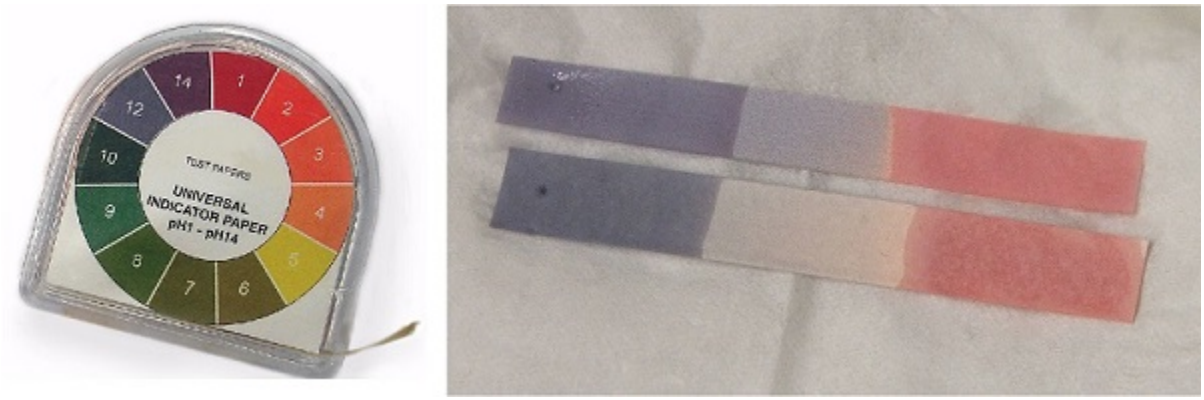


Figure 6.6.9: pH Paper. pH paper contains a set of indicators that change color at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the color to the standards provided. (CC BY-SA-NC; Anonymous by request)

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online
https://www.youtube.com/embed/1IqzUa5lABs?vq=hd1080

pH Indicators: pH Indicators(opens in new window) [youtu.be]

Summary and Takeaway

Plots of acid–base titrations generate titration curves that can be used to calculate the pH, the pOH, the pK_a, and the pK_b of the system. The shape of a titration curve, a plot of pH versus the amount of acid or base added, provides important information about what is occurring in solution during a titration. The shapes of titration curves for weak acids and bases depend dramatically on the identity of the compound. The equivalence point of an acid–base titration is the point at which exactly enough acid or base has been added to react completely with the other component. The equivalence point in the titration of a strong acid or a strong base occurs at pH 7.0. In titrations of weak acids or weak bases, however, the pH at the equivalence point is greater or less than 7.0, respectively. The pH tends to change more slowly before the equivalence point is reached in titrations of weak acids and weak bases than in titrations of strong acids and strong bases. The pH at the midpoint, the point halfway on the titration curve to the equivalence point, is equal to the pK_a of the weak acid or the pK_b of the weak base. Thus titration methods can be used to determine both the concentration and the pK_a (or the pK_b) of a weak acid (or a weak base). Acid–base indicators are compounds that change color at a particular pH. They are typically weak acids or bases whose changes in color correspond to deprotonation or protonation of the indicator itself.

6.6: Acid-Base Titration Curves is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

6.7: Polyprotic Acids

Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

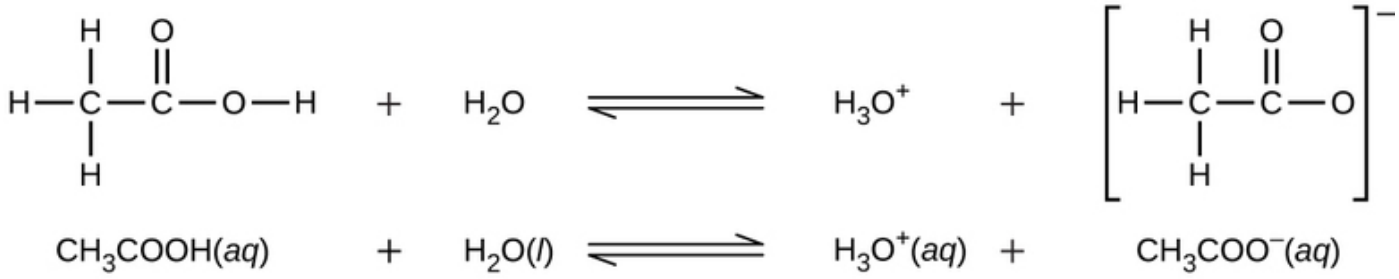
We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, $\mathrm{HNO_3}$, and HCN that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:

$$\mathrm{HCl}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{Cl^-}(aq)$$

$$\mathrm{HNO_3}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{NO_3{}^-}(aq)$$

$$\mathrm{HCN}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{CN^-}(aq)$$

Even though it contains four hydrogen atoms, acetic acid, $\mathrm{CH_3CO_2H}$, is also monoprotic because only the hydrogen atom from the carboxyl group ($-\mathrm{COOH}$) reacts with bases:



This image contains two equilibrium reactions. The first shows a C atom bonded to three H atoms and another C atom. The second C atom is double bonded to an O atom and also forms a single bond to another O atom. The second O atom is bonded to an H atom. There is a plus sign and then the molecular formula H subscript 2 O. An equilibrium arrow follows the H subscript 2 O. To the right of the arrow is H subscript 3 O superscript positive sign. There is a plus sign. The final structure shows a C atom bonded the three H atoms and another C atom. This second C atom is double bonded to an O atom and single bonded to another O atom. The entire structure is in brackets and a superscript negative sign appears outside the brackets. The second reaction shows C H subscript 3 C O O H (a q) plus H subscript 2 O (l) equilibrium arrow H subscript 3 O (a q) plus C H subscript 3 C O O superscript negative sign (a q).

Similarly, monoprotic bases are bases that will accept a single proton.

Diprotic Acids

Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

- **The first ionization is**

$$\mathrm{H_2SO_4}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HSO_4{}^-}(aq)$$

with $K_{\mathrm{a1}} > 10^2$; *complete dissociation.*

- **The second ionization is**

$$\mathrm{HSO_4{}^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4{}^{2-}}(aq)$$

with $K_{\mathrm{a2}} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids. When we make a solution of a weak diprotic acid, we get a solution that contains a mixture of acids. Carbonic acid, H_2CO_3, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

- **First Ionization**

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

with

$$K_{H_2CO_3} = \frac{[H3O+][HCO3-]}{[H2CO3]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

- **Second Ionization**

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

with

$$K_{HCO_3^-} = \frac{[H3O+][CO3^2-]}{[HCO3-]} = 4.7 \times 10^{-11}$$

$K_{H_2CO_3}$ is larger than $K_{HCO_3^-}$ by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that little of the HCO_3^- formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and HCO_3^- are practically equal in a pure aqueous solution of H_2CO_3.

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This can simplify our work considerably because we can determine the concentration of H_3O^+ and the conjugate base from the first ionization, then determine the concentration of the conjugate base of the second ionization in a solution with concentrations determined by the first ionization.

Example 6.7.1: Ionization of a Diprotic Acid

When we buy soda water (carbonated water), we are buying a solution of carbon dioxide in water. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are $[H_3O^+]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ in a saturated solution of CO_2 with an initial $[H_2CO_3] = 0.033\ M$?

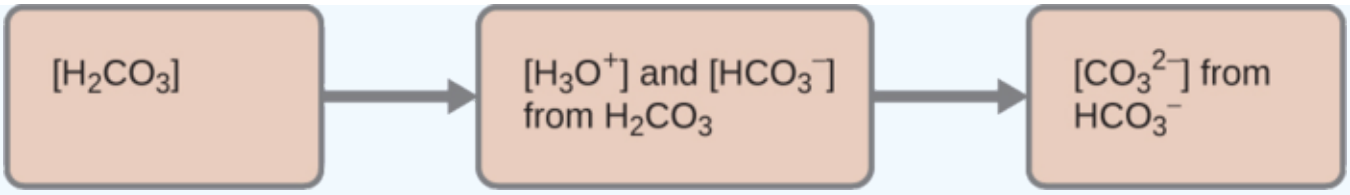
[redacted]

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than HCO_3^-, so H_2CO_3 is the dominant producer of hydronium ion in solution. Thus there are two parts in the solution of this problem:

1. Using the customary four steps, we determine the concentration of H_3O^+ and HCO_3^- produced by ionization of H_2CO_3.
2. Then we determine the concentration of CO_3^{2-} in a solution with the concentration of H_3O^+ and HCO_3^- determined in (1).

To summarize:



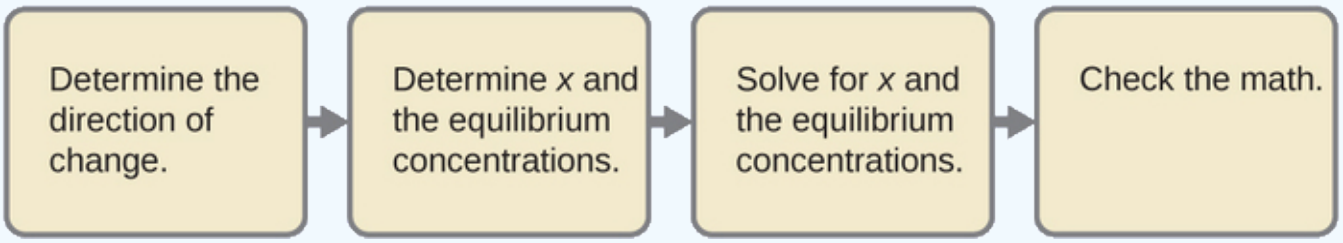
Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “left bracket H subscript 2 C O subscript 3 right bracket.” The second is labeled “left bracket H subscript 3 O superscript plus right bracket and left bracket H C O subscript 3 superscript negative right bracket from H subscript 2 C O subscript 3.” The third is labeled “left bracket C O subscript 3 superscript 2 negative right bracket from H C O subscript 3 superscript negative.”

1. First Ionization: Determine the concentrations of $\mathrm{H_3O^+}$ *and* $\mathrm{HCO_3^-}$.

Since equilibrium step 1 is has a much bigger $K_{a1} = 4.3 \times 10^{-7}$ than $K_{a2} = 4.7 \times 10^{-11}$ for equilibrium step 2, we can safely ignore the second ionization step and focus only on the first step (but address it in next part of problem).

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \quad K_{\mathrm{a1}} = 4.3 \times 10^{-7}$$

As for the ionization of any other weak acid:



Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “Determine the direction of change.” The second is labeled “Determine x and the equilibrium concentrations.” The third is labeled “Solve for x and the equilibrium concentrations.” The fourth is labeled “Check the math.”

An abbreviated table of changes and concentrations shows:

Abbreviated table of changes and concentrations

ICE Table	$\mathrm{H_2CO_3}(aq)$	$\mathrm{H_2O}(l)$	$\mathrm{H_3O^+}(aq)$	$\mathrm{HCO_3^-}(aq)$
Initial (M)	$0.033\ M$	-	0	0
Change (M)	$-x$	-	$+x$	$+x$
Equilibrium (M)	$0.033\ M - x$	-	x	x

Substituting the equilibrium concentrations into the equilibrium constant gives us:

$$K_{\mathrm{H_2CO_3}} = \frac{[H3O+][HCO3-]}{[H2CO3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Solving the preceding equation making our standard assumptions gives:

$$x = 1.2 \times 10^{-4}$$

Thus:

$$[\mathrm{H_2CO_3}] = 0.033\ M$$

$$[\mathrm{H_3O^+}] = [\mathrm{HCO_3^-}\ ] = 1.2 \times 10^{-4}\ M$$

2. Second Ionization: Determine the concentration of CO_3^{2-} in a solution at equilibrium.

Since the equilibrium step 1 is has a much bigger K_a than equilibrium step 2, we can the equilibrium conditions calculated from first part of example as the initial conditions for an ICER Table for the equilibrium step 2:

$$\mathrm{HCO_3}^-(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{CO_3}^{2-}(aq)$$

ICER Table for the equilibrium step 2:

ICE Table	$\mathrm{HCO_3}^-(aq)$	$\mathrm{H_2O}(l)$	$\mathrm{H_3O}^+(aq)$	$\mathrm{CO_3}^{2-}(aq)$
Initial (M)	$1.2 \times 10^{-4}\ M$	-	$1.2 \times 10^{-4}\ M$	0
Change (M)	$-y$	-	$+y$	$+y$
Equilibrium (M)	$1.2 \times 10^{-4}\ M - y$	-	$1.2 \times 10^{-4}\ M + y$	y

$$K_{\mathrm{HCO_3}^-} = \frac{[H3O+][CO3^2-]}{[HCO3-]} = \frac{(1.2 \times 10^{-4}\ M + y)(y)}{(1.2 \times 10^{-4}\ M - y)}$$

To avoid solving a quadratic equation, we can assume $y \ll 1.2 \times 10^{-4}\ M$ so

$$K_{\mathrm{HCO_3}^-} = 4.7 \times 10^{-11} \approx \frac{(1.2 \times 10^{-4}\ M)(y)}{(1.2 \times 10^{-4}\ M)}$$

Rearranging to solve for y

$$y \approx \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4}\ M)}{1.2 \times 10^{-4}\ M}$$

$$[\mathrm{CO_3}^{2-}] = y \approx 4.7 \times 10^{-11}$$

To summarize:

In part 1 of this example, we found that the $\mathrm{H_2CO_3}$ in a 0.033-*M* solution ionizes slightly and at equilibrium $[\mathrm{H_2CO_3}] = 0.033\ M$, $[\mathrm{H_3O}^+] = 1.2 \times 10^{-4}$, and $[\mathrm{HCO_3}^-] = 1.2 \times 10^{-4}\ M$. In part 2, we determined that $[\mathrm{CO_3}^{2-}] = 5.6 \times 10^{-11}\ M$.

Exercise 6.7.2: Hydrogen Sulfide

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 *M*. Calculate $[\mathrm{H_3O}^+]$, $[\mathrm{HS}^-]$, and $[\mathrm{S}^{2-}]$ in the solution:

$$\mathrm{H_2S}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{HS}^-(aq) \quad K_{\mathrm{a1}} = 8.9 \times 10^{-8}$$

$$\mathrm{HS}^-(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{S}^{2-}(aq) \quad K_{\mathrm{a2}} = 1.0 \times 10^{-19}$$

Answer

$$[\mathrm{H_2S}] = 0.1M,\ [\mathrm{H_3O}^+] = [HS^-] = 0.0001\ M,\ [S^{2-}] = 1 \times 10^{-19}\ M$$

> We note that the concentration of the sulfide ion is the same as K_{a2}. This is due to the fact that each subsequent dissociation occurs to a lesser degree (as acid gets weaker).

Triprotic Acids

A triprotic acid is an acid that has three dissociable protons that undergo stepwise ionization: Phosphoric acid is a typical example:

- **The first ionization is**

$$\mathrm{H_3PO_4}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{H_2PO_4^-}(aq)$$

with $K_{a1} = 7.5 \times 10^{-3}$.

- **The second ionization is**

$$\mathrm{H_2PO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HPO_4^{2-}}(aq)$$

with $K_{a2} = 6.2 \times 10^{-8}$.

- **The third ionization is**

$$\mathrm{HPO_4^{2-}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{PO_4^{3-}}(aq)$$

with $K_{a3} = 4.2 \times 10^{-13}$.

As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6. This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of H_3PO_4 complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6, the calculations can be broken down into a series of parts similar to those for diprotic acids.

Polyprotic bases can accept more than one hydrogen ion in solution. The carbonate ion is an example of a diprotic base, since it can accept up to two protons. Solutions of alkali metal carbonates are quite alkaline, due to the reactions:

$$\mathrm{H_2O}(l) + \mathrm{CO_3^{2-}}(aq) \rightleftharpoons \mathrm{HCO_3^-}(aq) + \mathrm{OH^-}(aq)$$

and

$$\mathrm{H_2O}(l) + \mathrm{HCO_3^-}(aq) \rightleftharpoons \mathrm{H_2CO_3}(aq) + \mathrm{OH^-}(aq)$$

Summary

An acid that contains more than one ionizable proton is a polyprotic acid. The protons of these acids ionize in steps. The differences in the acid ionization constants for the successive ionizations of the protons in a polyprotic acid usually vary by roughly five orders of magnitude. As long as the difference between the successive values of K_a of the acid is greater than about a factor of 20, it is appropriate to break down the calculations of the concentrations of the ions in solution into a series of steps.

Glossary

diprotic acid
: acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

diprotic base
: base capable of accepting two protons. The protons are accepted in two steps

monoprotic acid
acid containing one ionizable hydrogen atom per molecule

stepwise ionization
process in which an acid is ionized by losing protons sequentially

triprotic acid
acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

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6.8: A Deeper Look - Exact Treatment of Acid-Base Equilibria

Learning Objectives

- Understand the exact equations that are involves in complex acid-base equilibria in aqueous solutions

The methods for dealing with acid-base equilibria that we developed in the earlier units of this series are widely used in ordinary practice. Although many of these involve approximations of various kinds, the results are usually good enough for most purposes. Sometimes, however — for example, in problems involving very dilute solutions, the approximations break down, often because they ignore the small quantities of H^+ and OH^- ions always present in pure water. In this unit, we look at exact, or "comprehensive" treatment of some of the more common kinds of acid-base equilibria problems.

Strong acid-base systems

The usual definition of a “strong” acid or base is one that is completely dissociated in aqueous solution. Hydrochloric acid is a common example of a strong acid. When HCl gas is dissolved in water, the resulting solution contains the ions H_3O^+, OH^-, and Cl^-, but except in very concentrated solutions, the concentration of HCl is negligible; for all practical purposes, molecules of “hydrochloric acid”, HCl, do not exist in dilute aqueous solutions. To specify the concentrations of the three species present in an aqueous solution of HCl, we need three independent relations between them.

These relations are obtained by observing that certain conditions must **always** hold for aqueous solutions:

1. The dissociation equilibrium of water must always be satisfied:

   [redacted]

2. The undissociated acid and its conjugate base must be in *mass balance*. The actual concentrations of the acid and its conjugate base can depend on a number of factors, but their sum must be constant, and equal to the “nominal concentration”, which we designate here as C_a. For a solution of HCl, this equation would be

   [redacted]

   Because a strong acid is by definition completely dissociated, we can neglect the first term and write the mass balance condition as

   [redacted]

3. In any ionic solution, the sum of the positive and negative electric charges must be zero; in other words, all solutions are electrically neutral. This is known as the *electroneutrality principle*.

   [redacted]

The next step is to combine these three limiting conditions into a single expression that relates the hydronium ion concentration to C_a. This is best done by starting with an equation that relates several quantities and substituting the terms that we want to eliminate. Thus we can get rid of the $[Cl^-]$ term by substituting Equation 1.6.887 into Equation 6.8.1255 :

[redacted]

The $[OH^-]$ term can be eliminated by the use of Equation 1.6.884:

[redacted]

This equation tells us that the hydronium ion concentration will be the same as the nominal concentration of a strong acid as long as the solution is not very dilute. As the acid concentration falls below about 10^{-6} M, however, the second term predominates; $[H^+]$ approaches $\sqrt{K_w}$ or $10^{-7}M$ at 25 °C. The hydronium ion concentration can of course never fall below this value; no amount of dilution can make the solution alkaline!

> No amount of dilution can make the solution of a strong acid alkaline!

Notice that Equation 6.8.1257 is a quadratic equation; in regular polynomial form it would be rewritten as

[redacted]

Most practical problems involving strong acids are concerned with more concentrated solutions in which the second term of Equation 6.8.1258 can be dropped, yielding the simple relation

$$[H^+] \approx [A^-] \tag{6.8.1641}$$

In more concentrated solutions, interactions between ions cause their “effective” concentrations, known as their *activities*, to deviate from their “analytical” concentrations. Thus in a solution prepared by adding 0.5 mole of the very strong acid $HClO_4$ to sufficient water to make the volume 1 liter, freezing-point depression measurements indicate that the concentrations of hydronium and perchlorate ions are only about 0.4 *M*. This does not mean that the acid is only 80% dissociated; there is no evidence of $HClO_4$ molecules in the solution. What has happened is that about 20% of the H_3O^+ and ClO_4^- ions have formed ion-pair complexes in which the oppositely-charged species are loosely bound by electrostatic forces. Similarly, in a 0.10 *M* solution of hydrochloric acid, the activity of H^+ is 0.81, or only 81% of its concentration. (See the green box below for more on this.)

Activities are important because only these work properly in equilibrium calculations. The relation between the concentration of a species and its activity is expressed by the *activity coefficient* γ:

[redacted]

As a solution becomes more dilute, γ approaches unity. At ionic concentrations below about 0.001 *M*, concentrations can generally be used in place of activities with negligible error. Recall that pH is defined as the negative logarithm of the hydrogen ion *activity*, not its concentration.

> Activities of single ions cannot be determined, so activity coefficients in ionic solutions are always the average, or *mean*, of those for all ionic species present. This quantity is denoted as $\gamma_{\pm}$.

At very high concentrations, activities can depart wildly from concentrations. This is a practical consideration when dealing with strong mineral acids which are available at concentrations of 10 M or greater. In a 12 *M* solution of hydrochloric acid, for example, the mean ionic activity coefficient* is 207. This means that under these conditions with $[H^+]$ = 12, the activity $\{H^+\}$ = 2500, corresponding to a pH of about –3.4, instead of –1.1 as might be predicted if concentrations were being used. These very high activity coefficients also explain another phenomenon: why you can detect the odor of HCl over a concentrated hydrochloric acid solution even though this acid is supposedly "100% dissociated".

At these high concentrations, a pair of "dissociated" ions H^+ and Cl^- will occasionally find themselves so close together that they may momentarily act as an HCl unit; some of these may escape as \(HCl(g)\) before thermal motions break them up again. Under these conditions, “dissociation” begins to lose its meaning so that in effect, dissociation is no longer complete. Although the concentration of \(HCl(aq)\) will always be very small, its own activity coefficient can be as great as 2000, which means that its escaping tendency from the solution is extremely high, so that the presence of even a tiny amount is very noticeable.

Weak monoprotic acids and bases

Most acids are weak; there are hundreds of thousands of them, whereas there are no more than a few dozen strong acids. We can treat weak acid solutions in exactly the same general way as we did for strong acids. The only difference is that we must now include the equilibrium expression for the acid. We will start with the simple case of the pure acid in water, and then go from there to the more general one in which strong cations are present. In this exposition, we will refer to “hydrogen ions” and $[H^+]$

for brevity, and will assume that the acid HA dissociates into H^+ and its conjugate base A^-.

Pure acid in water

In addition to the species H^+, OH^-, and A– which we had in the strong-acid case, we now have the undissociated acid HA; four variables, requiring four equations.

- **Equilibria**

[redacted]

- **Mass balance**

[redacted]

- **Charge balance**

[redacted]

To eliminate [HA] from Equation 6.8.1261, we solve Equation 6.8.1263 for this term, and substitute the resulting expression into the numerator:

[redacted]

The latter equation is simplified by multiplying out and replacing $[H^+][OH^-]$ with K_w. We then get rid of the $[OH^-]$ term by replacing it with $K_w/[H^+]$

$$[H^+]C_b + [H^+]^2 - [H^+][OH^-] = K_aC_a - K_a[H^+] + K_a[OH^-] \tag{6.8.1642}$$

$$[H^+]^2C_b + [H^+]^3 - [H^+]K_w = K_aC_a - K_a[H^+] + \frac{K_aK_w}{[H^+]} \tag{6.8.1643}$$

Rearranged into standard polynomial form, this becomes

[redacted]

For most practical applications, we can make approximations that eliminate the need to solve a cubic equation.

Approximation 1: Neglecting Hydroxide Population

Unless the acid is extremely weak or the solution is very dilute, the concentration of OH^- can be neglected in comparison to that of $[H^+]$. If we assume that $[OH^-] \ll [H^+]$, then Equation 6.8.1267 can be simplified to

[redacted]

which is a quadratic equation:

[redacted]

and thus, from the quadratic formula,

[redacted]

Example 6.8.1: Acetic Acid

Calculate the pH of a 0.0010 M solution of acetic acid, $K_a = 1.74 \times 10^{-5}$.

Solution

First approximation:

$$[H^+] = \sqrt{(1.0 \times 10^{-3}) \times (1.74 \times 10^{-5}} = \sqrt{1.74 \times 10^{-8}} = 1.3 \times 10^{-4}\ M.$$

Applying the "5% test",

$$\frac{1.3 \times 10^{-4}}{1.0 \times 10^{-3}} = 0.13$$

This exceeds 0.05, so we must explicitly solve the quadratic Equation 6.8.1269 to obtain two roots: $+1.2 \times 10^{-4}$ and -1.4×10^{-4}. Taking the positive root, we have

$$pH = -\log(1.2 \times 10^{-4}) = 3.9$$

Approximation 2: Very Concentrated Acids

If the acid is fairly concentrated (usually more than 10^{-3} M), a further simplification can frequently be achieved by making the assumption that $[H^+] \ll C_a$. This is justified when most of the acid remains in its protonated form [HA], so that relatively little H^+ is produced. In this event, Equation 6.8.1268 reduces to

[redacted]

or

[redacted]

Example 6.8.2

Calculate the pH and percent ionization of 0.10 M acetic acid "HAc" (CH_3COOH), $K_a = 1.74 \times 10^{-5}$.

Solution

It is usually best to start by using Equation 6.8.1271 as a first approximation:

$$[H^+] = \sqrt{(0.10)(1.74 \times 10^{-5})} = \sqrt{1.74 \times 10^{-6}} = 1.3 \times 10^{-3}\ M$$

This approximation is generally considered valid if $[H^+]$ is less than 5% of C_a; in this case, $[H^+]/C_a$ = 0.013, which is smaller than 0.05 and thus within the limit. This same quantity also corresponds to the ionization fraction, so the percent ionization is 1.3%. The pH of the solution is

$$pH = -\log 1.2 \times 10^{-3} = 2.9$$

Approximation 3: Very Weak and Acidic

If the acid is very weak or its concentration is very low, the H^+ produced by its dissociation may be little greater than that due to

the ionization of water. However, if the solution is still acidic, it may still be possible to avoid solving the cubic equation 6.8.1267 by assuming that the term $([H^+] - [OH^-]) \ll C_a$ in Equation 6.8.1264:

[redacted]

This can be rearranged into standard quadratic form

[redacted]

For dilute solutions of weak acids, an exact treatment may be required. With the aid of a computer or graphic calculator, solving a cubic polynomial is now far less formidable than it used to be. However, round-off errors can cause these computerized cubic solvers to blow up; it is generally safer to use a quadratic approximation.

Example 6.8.3: Boric Acid

Boric acid, $B(OH)_3$ ("H_3BO_3") is a weak acid found in the ocean and in some natural waters. As with many boron compounds, there is some question about its true nature, but for most practical purposes it can be considered to be monoprotic with $K_a = 7.3 \times 10^{-10}$:

$$Bi(OH)_3 + 2H_2O \rightleftharpoons Bi(OH)_4^- + H_3O^+$$

Find the [H^+] and pH of a 0.00050 M solution of boric acid in pure water.

Solution

Because this acid is quite weak and its concentration low, we will use the quadratic form Equation 6.8.1269, which yields the positive root 6.12×10^{-7}, corresponding to pH = 6.21. Notice that this is only six times the concentration of H^+ present in pure water!

It is instructive to compare this result with what the quadratic approximation would yield, which yield $[H^+] = 6.04 \times 10^{-7}$ so $pH = 6.22$.

Weak bases

The weak bases most commonly encountered are:

- anions A^- of weak acids:

$$A^- + H_2O \rightleftharpoons HA + OH^- \tag{6.8.1644}$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \tag{6.8.1645}$$

- ammonia

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \tag{6.8.1646}$$

- amines, e.g. methylamine

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + H_2O \tag{6.8.1647}$$

Solution of an anion of a weak acid

Note that, in order to maintain electroneutrality, anions must be accompanied by sufficient cations to balance their charges. Thus for a C_b *M* solution of the salt NaA in water, we have the following conditions:

- **Species**

Na^+, A^-, HA, H_2O, H^+, OH^-

- **Equilibria**

- **Mass balance**

- **Charge balance**

Replacing the [Na^+] term in Equation 6.8.1281 by C_b and combining with K_w and the mass balance, a relation is obtained that is analogous to that of Equation 6.8.1264 for weak acids:

The approximations

and

can be derived in a similar manner.

Example 6.8.4: Methylamine

Calculate the pH and the concentrations of all species in a 0.01 M solution of methylamine, CH_3NH_2 ($K_b = 4.2 \times 10^{-4}$).

Solution

We begin by using the simplest approximation Equation 6.8.1280:

$$[OH^-] = \sqrt{(K_b C_b -} = \sqrt{(4.2 \times 10^{-4})(10^{-2})} = 2.1 \times 10^{-3}$$

To see if this approximation is justified, we apply a criterion similar to what we used for a weak acid: [OH^-] must not exceed 5% of C_b. In this case,

$$\frac{[OH^-]}{C_b} = \frac{(2.1 \times 10^{-3}}{10^{-2}} = 0.21$$

so we must use the quadratic form Equation 6.8.1274 that yields the positive root 1.9×10^{-3} which corresponds to $[OH^-]$

$$[H^+] = \frac{K_w}{[OH^-} = \frac{1 \times 10^{-14}}{1.9 \times 10^{-3}} = 5.3 \times 10^{-12}$$

and

$$pH = -\log 5.3 \times 10^{-12} = 11.3.$$

From the charge balance equation, solve for

$$[CH_3NH_2] = [OH^-]–[H^+] \approx [OH^-] = 5.3 \times 10^{-12}\ M.$$

For the concentration of the acid form (methylaminium ion $CH_3NH_3^+$), use the mass balance equation:

$$[CH_3NH_3^+] = C_b–[CH_3NH_2] = 0.01–0.0019 = 0.0081\ M.$$

Mixtures of Acids

Many practical problems relating to environmental and physiological chemistry involve solutions containing more than one acid. In this section, we will restrict ourselves to a much simpler case of two acids, with a view toward showing the general method of approaching such problems by starting with charge- and mass-balance equations and making simplifying assumptions when justified. In general, the hydrogen ions produced by the stronger acid will tend to suppress dissociation of the weaker one, and both will tend to suppress the dissociation of water, thus reducing the sources of H^+ that must be dealt with.

Consider a mixture of two weak acids HX and HY; their respective nominal concentrations and equilibrium constants are denoted by C_x, C_y, K_x and K_y,

Starting with the charge balance expression

We use the equilibrium constants to replace the conjugate base concentrations with expressions of the form

to yield

If neither acid is very strong or very dilute, we can replace equilibrium concentrations with nominal concentrations:

Example 6.8.5: Acetic Acid and Formic Acid

Estimate the pH of a solution that is 0.10M in acetic acid ($K_a = 1.8 \times 10^{-5}$) and 0.01M in formic acid ($K_a = 1.7 \times 10^{-4}$).

Solution

Because K_w is negligible compared to the C_aK_a products, we can simplify \Equation $ref3-4$:

$$[H^+] = \sqrt{1.8 \times 10^{-6} + 1.7 \times 10^{-6}} = 0.0019$$

Which corresponds to a pH of $-\log 0.0019 = 2.7$

Note that the pH of each acid separately at its specified concentration would be around 2.8. However, if 0.001 M chloroacetic acid (K_a= 0.0014) is used in place of formic acid, the above expression becomes

which exceeds the concentration of the stronger acid; because the acetic acid makes a negligible contribution to $[H^+]$ here, the simple approximation given above \Equation 6.8.1288 is clearly invalid. We now use the mass balance expression for the stronger acid

to solve for $[X^-]$ which is combined with the equilibrium constant K_x to yield

Solving this for $[X^-]$ gives

The approximation for the weaker acetic acid (HY) is still valid, so we retain it in the substituted electronegativity expression:

which is a cubic equation that can be solved by approximation.

Several methods have been published for calculating the hydrogen ion concentration in solutions containing an arbitrary number of acids and bases. These generally involve iterative calculations carried out by a computer. See, for example, *J. Chem. Education* 67(6) 501-503 (1990) and 67(12) 1036-1037 (1990).

Equilibria of Polyprotic Acids

Owing to the large number of species involved, exact solutions of problems involving polyprotic acids can become very complicated. Thus for phosphoric acid H_3PO_4, the three "dissociation" steps yield three conjugate bases:

$$H_3PO_4 \xrightarrow[10^{-2.12}]{K_1} H_2PO_4^- \xrightarrow[10^{-7.2}]{K_2} HPO_4^{2-} \xrightarrow[10^{-12.3}]{K_3} PO_4^{3-}$$

Fortunately, it is usually possible to make simplifying assumptions in most practical applications. In the section that follows, we will show how this is done for the less-complicated case of a diprotic acid. A diprotic acid HA can donate its protons in two steps, yielding first a monoprotonated species HA^- and then the completely deprotonated form A^{2-}.

$$H_2A \xrightarrow{K_1} HA^- \xrightarrow{K_2} A^{2-}$$

Since there are five unknowns (the concentrations of the acid, of the two conjugate bases and of H^+ and OH^-), we need five equations to define the relations between these quantities. These are

- **Equilibria**

- **Mass balance**

- **Charge balance**

[redacted]

(It takes 2 moles of H^+ to balance the charge of 1 mole of A^{2-})

Solving these five equations simultaneously for K_1 yields the rather intimidating expression

[redacted]

which is of little practical use except insofar as it provides the starting point for various simplifying approximations.

If the solution is even slightly acidic, then ($[H^+] - [OH^-]$) ≈ $[H^+]$ and

[redacted]

For any of the common diprotic acids, K_2 is much smaller than K_1. If the solution is sufficiently acidic that $K_2 \ll [H^+]$, then a further simplification can be made that removes K_2 from Equation 6.8.1301; this is the starting point for most practical calculations.

[redacted]

Finally, if the solution is sufficiently concentrated and K_1 sufficiently small so that $[H^+] \ll C_a$, then Equation 6.8.1302 reduces to:

$$[H^+] \approx \sqrt{K_a C_a} \tag{6.8.1648}$$

Acid with conjugate base: Buffer solutions

Solutions containing a weak acid together with a salt of the acid are collectively known as *buffers*. When they are employed to control the pH of a solution (such as in a microbial growth medium), a sodium or potassium salt is commonly used and the concentrations are usually high enough for the Henderson-Hasselbalch equation to yield adequate results.

Exact solution

In this section, we will develop an exact analytical treatment of weak acid-salt solutions, and show how the H¯H equation arises as an approximation. A typical buffer system is formed by adding a quantity of strong base such as sodium hydroxide to a solution of a weak acid HA. Alternatively, the same system can be made by combining appropriate amounts of a weak acid and its salt NaA. A system of this kind can be treated in much the same way as a weak acid, but now with the parameter C_b in addition to C_a.

- **Species**

Na^+, A^-, HA, H_2O, H^+, OH^-

- **Equilibria**

[redacted]

[redacted]

- **Mass balance**

[redacted]

[redacted]

- **Charge balance**

[redacted]

Substituting Equation 6.8.1307 into Equation 6.8.1308 yields an expression for [A^-]:

Inserting this into Equation 6.8.1306 and solving for [HA] yields

Finally, we substitute these last two expressions into the equilibrium constant (Equation 6.8.1305):

which becomes cubic in [H^+] when [OH^-] is replaced by (K_w / [H^+]).

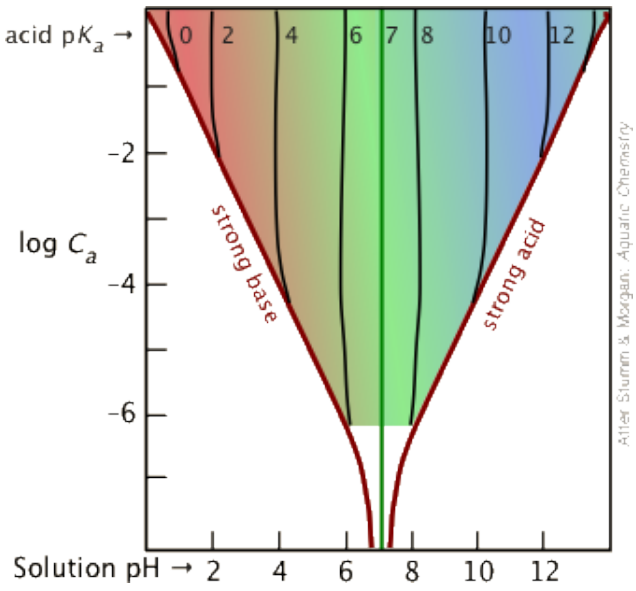
Approximations

In almost all practical cases it is possible to make simplifying assumptions. Thus if the solution is known to be acidic or alkaline, then the [OH^-] or [H^+] terms in Equation 6.8.1311 can be neglected. In acidic solutions, for example, Equation 6.8.1311 becomes

which can be rearranged into a quadratic in standard polynomial form:

If the concentrations C_a and C_b are sufficiently large, it may be possible to neglect the [H^+] terms entirely, leading to the commonly-seen *Henderson-Hasselbalch Approximation*.

It's important to bear in mind that the Henderson-Hasselbalch Approximation is an "approximation of an approximation" that is generally valid only for combinations of K_a and concentrations that fall within the colored portion of this plot.



Most buffer solutions tend to be fairly concentrated, with C_a and C_b typically around 0.01 - 0.1 *M*. For more dilute buffers and larger K_a's that bring you near the boundary of the colored area, it is safer to start with Equation 6.8.1313.

Example 6.8.6: Chlorous Acid Buffer

Chlorous acid $HClO_2$ has a pK_a of 1.94. Calculate the pH of a solution made by adding 0.01 M/L of sodium hydroxide to a -.02 M/L solution of chloric acid.

Solution

In the resulting solution, $C_a = C_b = 0.01M$. On the plots shown above, the intersection of the log C_a = –2 line with the plot for pK_a = 2 falls near the left boundary of the colored area, so we will use the quadratic form 6.8.1314.

Substitution in Equation 6.8.1314 yields

$$H^+ + 0.02H^+ - (10^{-1.9} x 10^{-2}) = 0$$

which yields a positive root 0.0047 = [H^+] that corresponds to pH = **2.3**.

Note: Using the Henderson-Hassalbach Approximateion (Equation 6.8.1315) would give pH = pK_a = 1.9.

6.8: A Deeper Look - Exact Treatment of Acid-Base Equilibria is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

6.9: Organic Acids and Bases - Structure and Reactivity

Learning Objectives

- To understand how molecular structure affects the strength of an acid or base.

We have seen that the strengths of acids and bases vary over many orders of magnitude. In this section, we explore some of the structural and electronic factors that control the acidity or basicity of a molecule.

Bond Strengths

In general, the stronger the $\mathrm{A{-}H}$ or $\mathrm{B{-}H^+}$ bond, the less likely the bond is to break to form H^+ ions and thus the less acidic the substance. This effect can be illustrated using the hydrogen halides:

Relative Acid Strength	HF	HCl	HBr	HI
H–X Bond Energy (kJ/mol)	570	432	366	298
pKa	3.20	−6.1	−8.9	−9.3

The trend in bond energies is due to a steady decrease in overlap between the 1s orbital of hydrogen and the valence orbital of the halogen atom as the size of the halogen increases. The larger the atom to which H is bonded, the weaker the bond. Thus the bond between H and a large atom in a given family, such as I or Te, is weaker than the bond between H and a smaller atom in the same family, such as F or O. As a result, acid strengths of binary hydrides increase as we go down a column of the periodic table. For example, the order of acidity for the binary hydrides of Group 16 elements is as follows, with pK_a values in parentheses:

[redacted]

Stability of the Conjugate Base

Whether we write an acid–base reaction as $AH \rightleftharpoons A^- + H^+$ or as $BH^+ \rightleftharpoons B + H^+$, the conjugate base ($A^-$ or B) contains one more lone pair of electrons than the parent acid (AH or BH^+). Any factor that stabilizes the lone pair on the conjugate base favors dissociation of H^+ and makes the parent acid a stronger acid. Let's see how this explains the relative acidity of the binary hydrides of the elements in the second row of the periodic table. The observed order of increasing acidity is the following, with pKa values in parentheses:

[redacted]

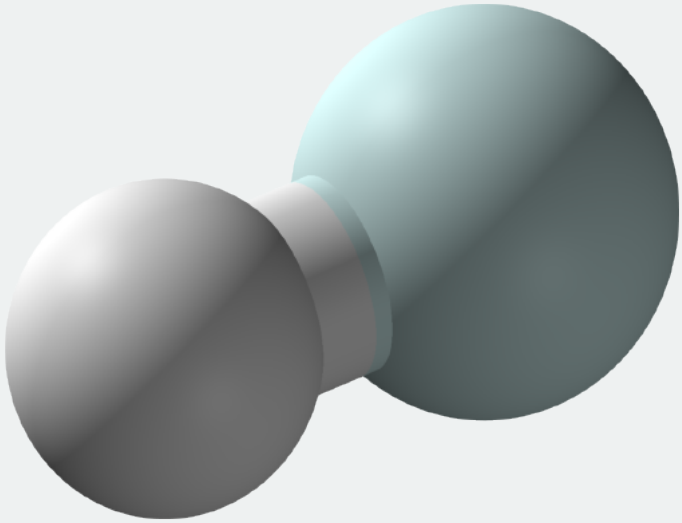
Consider, for example, the compounds at both ends of this series: methane and hydrogen fluoride. The conjugate base of CH_4 is CH_3^-, and the conjugate base of HF is F^-. Because fluorine is much more electronegative than carbon, fluorine can better stabilize the negative charge in the F^- ion than carbon can stabilize the negative charge in the CH3– ion. Consequently, HF has a greater tendency to dissociate to form H^+ and F^- than does methane to form H^+ and CH_3^-, making HF a much stronger acid than CH_4.

The same trend is predicted by analyzing the properties of the conjugate acids. For a series of compounds of the general formula HE, as the electronegativity of E increases, the E–H bond becomes more polar, favoring dissociation to form E^- and H^+. Due to both the increasing stability of the conjugate base and the increasing polarization of the E–H bond in the conjugate acid, acid strengths of binary hydrides increase as we go from left to right across a row of the periodic table.

Acid strengths of binary hydrides increase as we go down a column or from left to right across a row of the periodic table.

the strongest acid Known: The hydrohelium Cation

The stornger acid, the weaker the covalent bond to a hydrogen atom. So the strongest acid possible is the molecule with the weakest bond. That is the hydrohelium (1+) cation, $\mathrm{HeH^+}$, which is a positively charged ion formed by the reaction of a proton with a helium atom in the gas phase. It was first produced in the laboratory in 1925 and is isoelectronic with molecular hydrogen (\ce{H2}). It is the strongest known acid, with a proton affinity of 177.8 kJ/mol.



Ball and stick model of the hydrohelium ion. (CC BY-SA 3.0; CCoil).

$\mathrm{HeH^+}$ cannot be prepared in a condensed phase, as it would protonate any anion, molecule or atom with which it were associated. However it is possible to estimate a *hypothetical* aqueous acidity using Hess's law:

$HHe^+(g)$	→	$H^+(g)$	+ He(g)	+178 kJ/mol
$HHe^+(aq)$	→	$HHe^+(g)$		+973 kJ/mol
$H^+(g)$	→	$H^+(aq)$		−1530 kJ/mol
He(g)	→	He(aq)		+19 kJ/mol
$HHe^+(aq)$	→	$H^+(aq)$	+ He(aq)	−360 kJ/mol

A free energy change of dissociation of −360 kJ/mol is equivalent to a pK_a of −63.

It has been suggested that $\mathrm{HeH^+}$ should occur naturally in the interstellar medium, but it has not yet been detected.

Inductive Effects

Atoms or groups of atoms in a molecule other than those to which H is bonded can induce a change in the distribution of

electrons within the molecule. This is called an inductive effect, and, much like the coordination of water to a metal ion, it can have a major effect on the acidity or basicity of the molecule. For example, the hypohalous acids (general formula HOX, with X representing a halogen) all have a hydrogen atom bonded to an oxygen atom. In aqueous solution, they all produce the following equilibrium:



The acidities of these acids vary by about three orders of magnitude, however, due to the difference in electronegativity of the halogen atoms:

HOX	Electronegativity of X	pKa
HOCl	3.0	7.40
HOBr	2.8	8.55
HOI	2.5	10.5

As the electronegativity of X increases, the distribution of electron density within the molecule changes: the electrons are drawn more strongly toward the halogen atom and, in turn, away from the H in the O–H bond, thus weakening the O–H bond and allowing dissociation of hydrogen as H^+.

The acidity of oxoacids, with the general formula $HOXO_n$ (with n = 0–3), depends strongly on the number of terminal oxygen atoms attached to the central atom X. As shown in Figure $6.9.1$, the K_a values of the oxoacids of chlorine increase by a factor of about 10^4 to 10^6 with each oxygen as successive oxygen atoms are added. The increase in acid strength with increasing number of terminal oxygen atoms is due to both an inductive effect and increased stabilization of the conjugate base.

> Any inductive effect that withdraws electron density from an O–H bond increases the acidity of the compound.

Because oxygen is the second most electronegative element, adding terminal oxygen atoms causes electrons to be drawn away from the O–H bond, making it weaker and thereby increasing the strength of the acid. The colors in Figure $6.9.1$ show how the electrostatic potential, a measure of the strength of the interaction of a point charge at any place on the surface of the molecule, changes as the number of terminal oxygen atoms increases. In Figure $6.9.1$ and Figure $6.9.2$, blue corresponds to low electron densities, while red corresponds to high electron densities. The oxygen atom in the O–H unit becomes steadily less red from $HClO$ to $HClO_4$ (also written as $HOClO_3$, while the H atom becomes steadily bluer, indicating that the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. The decrease in electron density in the O–H bond weakens it, making it easier to lose hydrogen as H^+ ions, thereby increasing the strength of the acid.

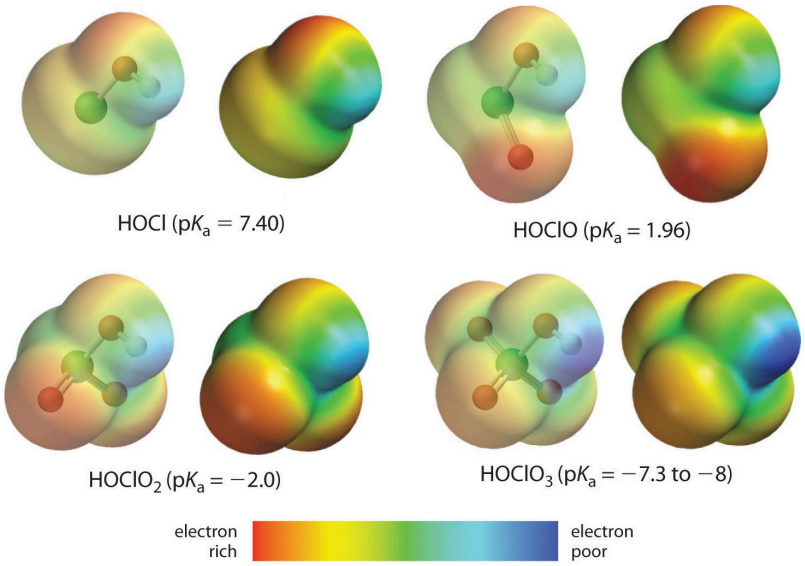
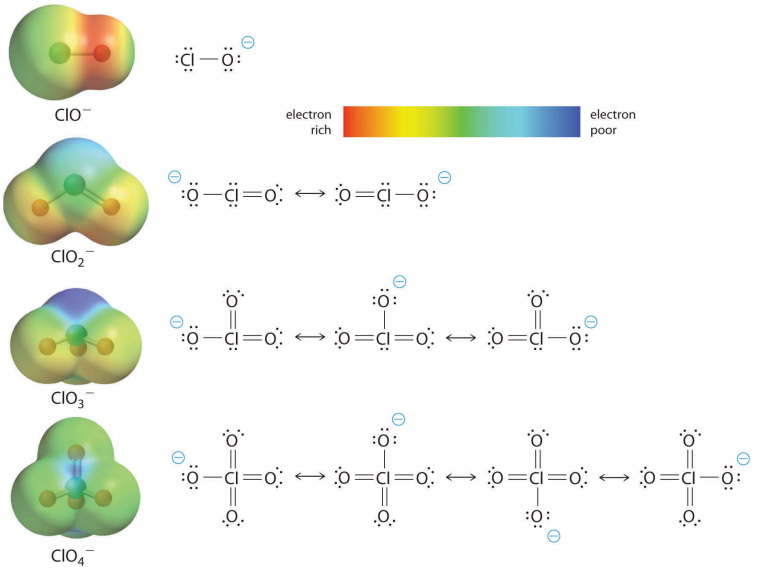


Figure 6.9.1: The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the O–H Unit. These electrostatic potential maps show how the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. Blue corresponds to low electron densities, whereas red corresponds to high electron densities. Source: Chlorine oxoacids pKa values from J. R. Bowser, Inorganic Chemistry (Pacific Grove, CA: Brooks-Cole,1993).

At least as important, however, is the effect of delocalization of the negative charge in the conjugate base. As shown in Figure 6.9.2, the number of resonance structures that can be written for the oxoanions of chlorine increases as the number of terminal oxygen atoms increases, allowing the single negative charge to be delocalized over successively more oxygen atoms.

Electron delocalization in the conjugate base increases acid strength.

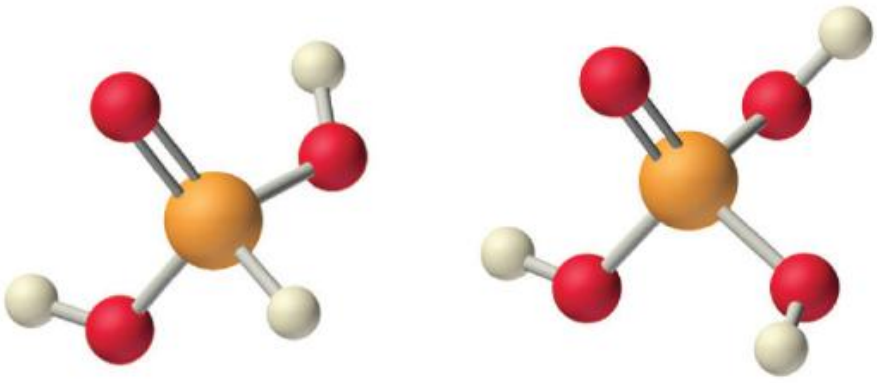
The electrostatic potential plots in Figure 6.9.2 demonstrate that the electron density on the terminal oxygen atoms decreases steadily as their number increases. The oxygen atom in ClO– is red, indicating that it is electron rich, and the color of oxygen progressively changes to green in ClO_4^+, indicating that the oxygen atoms are becoming steadily less electron rich through the series. For example, in the perchlorate ion (ClO_4^-), the single negative charge is delocalized over all four oxygen atoms, whereas in the hypochlorite ion (OCl^-), the negative charge is largely localized on a single oxygen atom (Figure 6.9.2). As a result, the perchlorate ion has no localized negative charge to which a proton can bind. Consequently, the perchlorate anion has a much lower affinity for a proton than does the hypochlorite ion, and perchloric acid is one of the strongest acids known.



As the number of terminal oxygen atoms increases, the number of resonance structures that can be written for the oxoanions of

chlorine also increases, and the single negative charge is delocalized over more oxygen atoms. As these electrostatic potential plots demonstrate, the electron density on the terminal oxygen atoms decreases steadily as their number increases. As the electron density on the oxygen atoms decreases, so does their affinity for a proton, making the anion less basic. As a result, the parent oxoacid is more acidic.

Similar inductive effects are also responsible for the trend in the acidities of oxoacids that have the same number of oxygen atoms as we go across a row of the periodic table from left to right. For example, H_3PO_4 is a weak acid, H_2SO_4 is a strong acid, and $HClO_4$ is one of the strongest acids known. The number of terminal oxygen atoms increases steadily across the row, consistent with the observed increase in acidity. In addition, the electronegativity of the central atom increases steadily from P to S to Cl, which causes electrons to be drawn from oxygen to the central atom, weakening the $\mathrm{O{-}H}$ bond and increasing the strength of the oxoacid.



Careful inspection of the data in Table $6.9.1$ shows two apparent anomalies: carbonic acid and phosphorous acid. If carbonic acid (H_2CO_3) were a discrete molecule with the structure $\mathrm{(HO)_2C{=}O}$, it would have a single terminal oxygen atom and should be comparable in acid strength to phosphoric acid (H_3PO_4), for which pKa1 = 2.16. Instead, the tabulated value of pK_{a1} for carbonic acid is 6.35, making it about 10,000 times weaker than expected. As we shall see, however, H_2CO_3 is only a minor component of the aqueous solutions of CO_2 that are referred to as carbonic acid. Similarly, if phosphorous acid (H_3PO_3) actually had the structure $(HO)_3P$, it would have no terminal oxygen atoms attached to phosphorous. It would therefore be expected to be about as strong an acid as $HOCl$ (pKa = 7.40). In fact, the pK_{a1} for phosphorous acid is 1.30, and the structure of phosphorous acid is $\mathrm{(HO)_2P(=O)H}$ with one H atom directly bonded to P and one $\mathrm{P{=}O}$ bond. Thus the pKa1 for phosphorous acid is similar to that of other oxoacids with one terminal oxygen atom, such as H_3PO_4. Fortunately, phosphorous acid is the only common oxoacid in which a hydrogen atom is bonded to the central atom rather than oxygen.

Table $6.9.1$: Values of pKa for Selected Polyprotic Acids and Bases

Polyprotic Acids	Formula	pK_{a1}	pK_{a2}	pK_{a3}
carbonic acid*	"H_2CO_3"	6.35	10.33	
citric acid	$HO_2CCH-2C(OH)(CO_2H)CH_2CO_2H$	3.13	4.76	6.40
malonic acid	$HO-2CCH_2CO_2H$	2.85	5.70	
oxalic acid	HO_2CCO_2H	1.25	3.81	
phosphoric acid	H_3PO_4	2.16	7.21	12.32
phosphorous acid	H_3PO_3	1.3	6.70	

***H_2CO_3 and H_2SO_3 are at best minor components of aqueous solutions of $CO_{2(g)}$ and $SO_{2(g)}$, respectively, but such solutions are commonly referred to as containing carbonic acid and sulfurous acid, respectively.**

Polyprotic Acids	Formula	pK_{a1}	pK_{a2}	pK_{a3}
succinic acid	$HO_2CCH_2CH_2CO_2H$	4.21	5.64	
sulfuric acid	H_2SO_4	–2.0	1.99	
sulfurous acid*	"H_2SO_3"	1.85	7.21	
Polyprotic Bases	**Formula**	pK_{b1}	pK_{b2}	
ethylenediamine	$H_2N(CH_2)_2NH_2$	4.08	7.14	
piperazine	$HN(CH_2CH_2)_2NH$	4.27	8.67	
propylenediamine	$H_2N(CH_2)_3NH_2$	3.45	5.12	

***H_2CO_3 and H_2SO_3 are at best minor components of aqueous solutions of $CO_{2(g)}$ and $SO_{2(g)}$, respectively, but such solutions are commonly referred to as containing carbonic acid and sulfurous acid, respectively.**

Inductive effects are also observed in organic molecules that contain electronegative substituents. The magnitude of the electron-withdrawing effect depends on both the nature and the number of halogen substituents, as shown by the pKa values for several acetic acid derivatives:

\[pK_a CH_3CO_2H 4.76< CH_2ClCO_2H 2.87

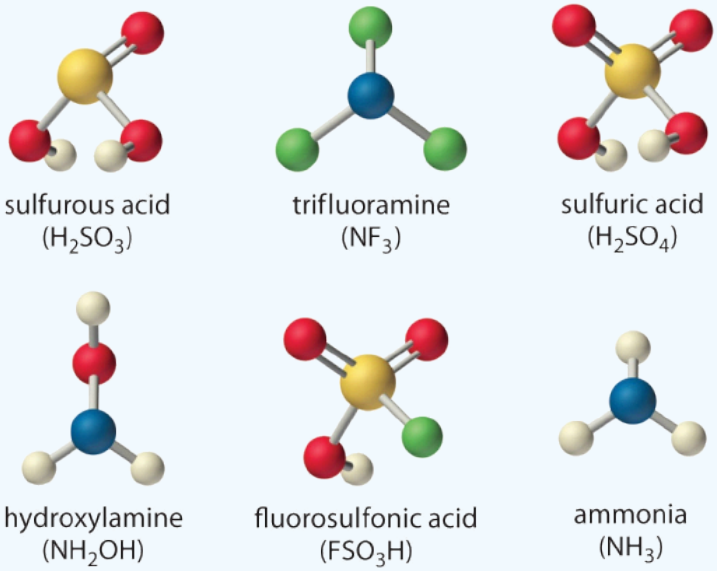
As you might expect, fluorine, which is more electronegative than chlorine, causes a larger effect than chlorine, and the effect of three halogens is greater than the effect of two or one. Notice from these data that inductive effects can be quite large. For instance, replacing the $-\mathrm{CH_3}$ group of acetic acid by a $-\mathrm{CF_3}$ group results in about a 10,000-fold increase in acidity!

Example 6.9.1

Arrange the compounds of each series in order of increasing acid or base strength.

a. sulfuric acid [H_2SO_4, or $(HO)_2SO_2$], fluorosulfonic acid (FSO_3H, or FSO_2OH), and sulfurous acid [H_2SO_3, or $(HO)_2SO$]
b. ammonia (NH_3), trifluoramine (NF_3), and hydroxylamine (NH_2OH)

The structures are shown here.



Given: series of compounds

Asked for: relative acid or base strengths

Strategy:

Use relative bond strengths, the stability of the conjugate base, and inductive effects to arrange the compounds in order of increasing tendency to ionize in aqueous solution.

Solution:

Although both sulfuric acid and sulfurous acid have two –OH groups, the sulfur atom in sulfuric acid is bonded to two terminal oxygen atoms versus one in sulfurous acid. Because oxygen is highly electronegative, sulfuric acid is the stronger acid because the negative charge on the anion is stabilized by the additional oxygen atom. In comparing sulfuric acid and fluorosulfonic acid, we note that fluorine is more electronegative than oxygen. Thus replacing an –OH by –F will remove more electron density from the central S atom, which will, in turn, remove electron density from the S–OH bond and the O–H bond. Because its O–H bond is weaker, FSO_3H is a stronger acid than sulfuric acid. The predicted order of acid strengths given here is confirmed by the measured pKa values for these acids:

\[pKa H_2SO_3 1.85

The structures of both trifluoramine and hydroxylamine are similar to that of ammonia. In trifluoramine, all of the hydrogen atoms in NH3 are replaced by fluorine atoms, whereas in hydroxylamine, one hydrogen atom is replaced by OH. Replacing the three hydrogen atoms by fluorine will withdraw electron density from N, making the lone electron pair on N less available to bond to an H^+ ion. Thus NF_3 is predicted to be a much weaker base than NH_3. Similarly, because oxygen is more electronegative than hydrogen, replacing one hydrogen atom in NH_3 by OH will make the amine less basic. Because oxygen is less electronegative than fluorine and only one hydrogen atom is replaced, however, the effect will be smaller. The predicted order of increasing base strength shown here is confirmed by the measured pK_b values:

\[pK_bNF_3—<

Trifluoramine is such a weak base that it does not react with aqueous solutions of strong acids. Hence its base ionization constant has never been measured.

Exercise 6.9.1

Arrange the compounds of each series in order of

a. decreasing acid strength: H_3PO_4, $CH_3PO_3H_2$, and $HClO_3$.
b. increasing base strength: CH_3S^-, OH^-, and CF_3S^-.

Answer a

$$HClO - 3 > CH_3PO_3H_2 > H_3PO_4$$

Answer a

$$CF_3S^- < CH_3S^- < OH^-$$

Summary

Inductive effects and charge delocalization significantly influence the acidity or basicity of a compound. The acid–base strength

of a molecule depends strongly on its structure. The weaker the A–H or B–H+ bond, the more likely it is to dissociate to form an H^+ ion. In addition, any factor that stabilizes the lone pair on the conjugate base favors the dissociation of H^+, making the conjugate acid a stronger acid. Atoms or groups of atoms elsewhere in a molecule can also be important in determining acid or base strength through an inductive effect, which can weaken an $\mathrm{O{-}H}$ bond and allow hydrogen to be more easily lost as H^+ ions.

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6.10: Lewis Bases as Nucleophilic Reactants in Organic Reactions

The basis of chemistry is that opposite charges attract and like charges repel, and that in reactions, electrons flow from “electron rich” areas to “electron poor” areas. A **name** to the types of species that are considered **“**electron rich**“** and “electron poor”. They are called **nucleophiles** and **electrophiles.**

Nucleophiles

A nucleophiles (from “nucleus loving”, or “positive-charge loving”) is **a reactant that provides a pair of electrons to form a new covalent bond.** This is the exact definition of a Lewis base discussed earlier. Hence, **nucleophiles are Lewis bases**. When the nucleophile donates a pair of electrons to a proton, it’s called a Brønsted base, or simply, “base”. As you can see, nucleophiles all have pairs of electrons to donate, and tend to be rich in electrons. Here are some examples of Lewis bases you are probably familiar with.

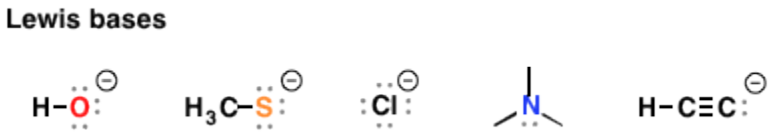


Figure 6.10.1: Examples of Lewis bases

When the nucleophile donates a pair of electrons to a **proton**, it’s called a Brønsted base.

How is nucleophilicity different from basicity? Well, since it’s not limited to simply forming a bond to hydrogen anymore, this leads to some extra complications. Let’s just talk about the measurement problem first. Many reactions of nucleophiles are not reversible. A bond forms, a bond breaks, and that’s the end of the reaction. The problem with this from a measurement standpoint is that we often cannot determine an equilibrium constant for a reaction. And if we can’t do that, then we cannot develop a reactivity scale based on equilibria. If we can’t measure equilibria, then what do we do? Well, we use the next best measurement available: to measure reaction **rates**, but that is discuss in the following chapters.

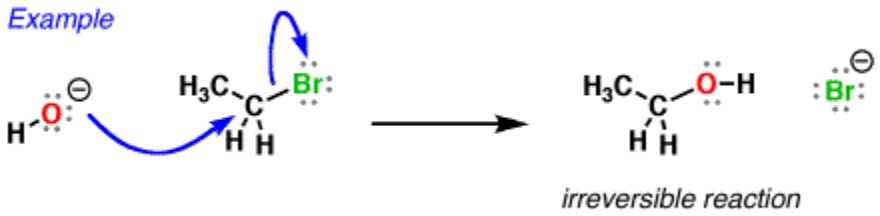


Figure 6.10.2: A nucleophilic reaction with a nucleophile donating a pair of electrons to the the carbon

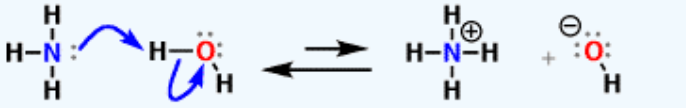
Example 6.10.1: Basicity in Organic Chemistry Reactions

So how do reactions of nucleophiles at hydrogen differ from reactions of nucleophiles at carbon? Well, they’re more easily reversible, for one thing. We can measure acidity (and, by extension, basicity) through the measure known as pKa, which is a reflection of the position of the equilibrium between an acid and its conjugate base.

What's a base?

- A base donates a pair of electrons to a proton

Example



How do we measure basicity?

- Because most species can participate in reversible acid-base reactions, we can measure basicity by the position of an *equilibrium*.
- In other words, we're measuring *relative stability* of the species involved. "Stability" is a *thermodynamic* property.

Acid-base reactions reflect relative stabilities

We can vaguely define “nucleophilicity” as “the extent to which a species can donate a pair of electrons”. A more precise definition will be discussed in organic chemistry courses.

Electrophilicity

Similarly, the extent to which a species can accept a lone pair of electrons is called “electrophilicity”. An electrophile (from “electron-loving”, or “negative-charge loving”) is a species that accepts a pair of electrons to form a new covalent bond. Again, this should sound familiar: this is the definition of a **Lewis acid**. An electrophile that accepts an electron pair at hydrogen is called a **Brønsted acid**, or just “acid”. Here are some examples of Lewis acids you’re familiar with.

Lewis acids

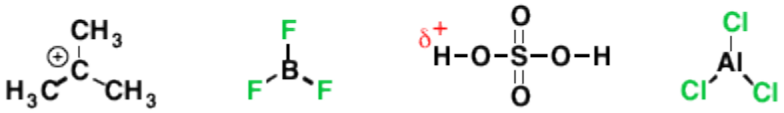


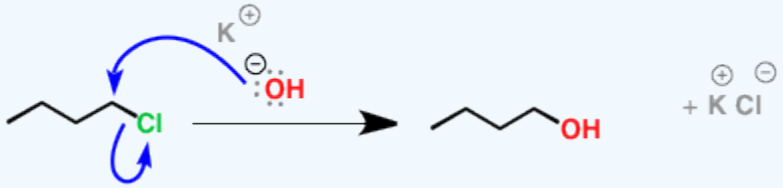
Figure 6.10.3: Lewis acids

Lewis acidity is essentially electrophilicity. Acidity (Brønsted acidity) is what we call it when the electrophile is a **proton**.

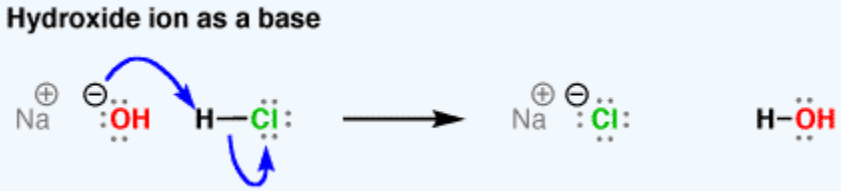
Example 6.10.1: The Hydroxide Ion

When hydroxide ion donates a pair of electrons to an electrophilic atom (such as carbon here) to form a new covalent bond, it is acting as a nucleophile.

Hydroxide ion as a nucleophile



And as we've seen before, when hydroxide ion donates a pair of electrons to an (acidic) proton to form a new covalent bond, we say it's acting as a "base".



The vast majority of the reactions you'll see in organic chemistry (>95%) – will be reactions where a nucleophile donates a pair of electrons to an electrophile (i.e., a nucleophile attacks an electrophile) with very few exceptions! This is why understanding where electrons are, and how electrons flow is so important – because the electron richness (or poorness) of an atom (or molecule) determines its nucleophilicity or electrophilicity, which in turn determines its reactivity. It's not an exaggeration to say that nucleophilicity and electrophilicity (and hence Lewis Acids and Bases) are the fundamental basis of chemical reactivity.

Summary

Basicity is a *subset* of nucleophilicity. While, all nucleophiles are Lewis bases since they donate a lone pair of electrons. A (Brønsted) base is the name we give to a nucleophile since it forms a bond to a proton (H^+). To summarize, when we're talking about basicity and nucleophilicity, we're talking about these two types of events.

Contributors and Attributions

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7.1: The Nature of Solubility Equilibria

Learning Objectives

- Understand the qualitative nature of dissolving a salt in water

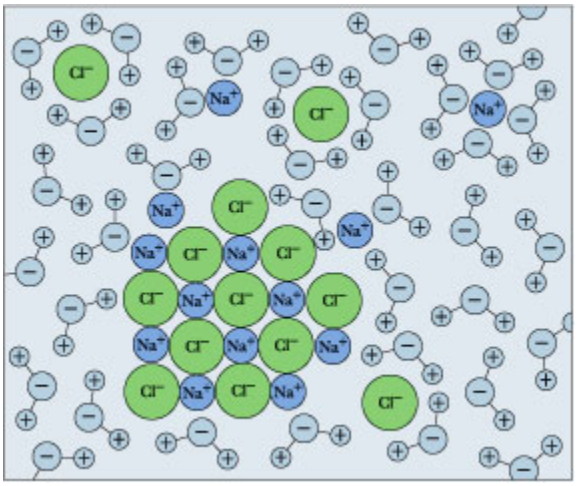
Dissolution of a salt in water is a chemical process that is governed by the same laws of chemical equilibrium that apply to any other reaction. There are, however, a number of special aspects of of these equilibria that set them somewhat apart from the more general ones that are covered in the lesson set devoted specifically to chemical equilibrium. These include such topics as the common ion effect, the influence of pH on solubility, supersaturation, and some special characteristics of particularly important solubility systems... all explained in what follows.

The Dissolution of Salts in Water

Drop some ordinary table salt into a glass of water, and watch it "disappear". We refer to this as *dissolution*, and we explain it as a process in which the sodium and chlorine units break away from the crystal surface, get surrounded by H_2O molecules, and become *hydrated ions*.

$$NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)} \tag{7.1.1649}$$

The designation *(aq)* means "aqueous" and comes from *aqua*, the Latin word for water. It is used whenever we want to emphasize that the ions are hydrated — that H_2O molecules are attached to them.



Remember that solubility equilibrium and the calculations that relate to it are only meaningful when *both* sides (solids and dissolved ions) are simultaneously present. But if you keep adding salt, there will come a point at which it no longer seems to dissolve. If this condition persists, we say that the salt has reached its s*olubility limit*, and the solution is s*aturated* in NaCl. The situation is now described by

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)} \tag{7.1.1650}$$

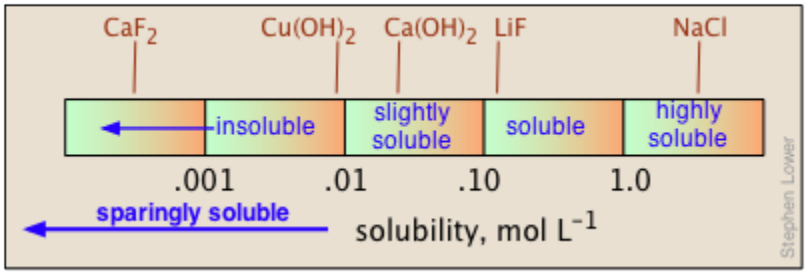
in which the solid and its ions are *in equilibrium*.

Salt solutions that have reached or exceeded their solubility limits (usually 36-39 g per 100 mL of water) are responsible for prominent features of the earth's geochemistry. They typically form when NaCl leaches from soils into waters that flow into salt lakes in arid regions that have no natural outlets; subsequent evaporation of these brines force the above equilibrium to the left, forming natural salt deposits. These are often admixed with other salts, but in some cases are almost pure NaCl. Many parts of

the world contain buried deposits of NaCl (known as halite) that formed from the evaporation of ancient seas, and which are now mined.

Expressing solubilities

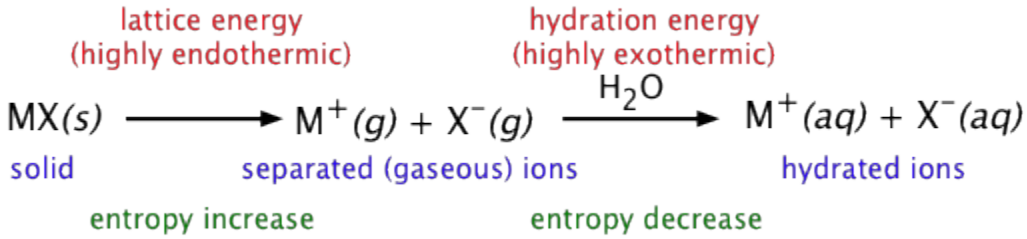
Solubilities are most fundamentally expressed in molar (mol L^{-1} of solution) or molal (mol kg^{-1} of water) units. But for practical use in preparing stock solutions, chemistry handbooks usually express solubilities in terms of grams-per-100 ml of water at a given temperature, frequently noting the latter in a superscript. Thus 6.9^{20} means 6.9 g of solute will dissolve in 100 mL of water at 20° C.



When quantitative data are lacking, the designations "soluble", "insoluble", "slightly soluble", and "highly soluble" are used. There is no agreed-on standard for these classifications, but a useful guideline might be that shown below.

What determines solubility?

The solubilities of salts in water span a remarkably large range of values, from almost completely insoluble to highly soluble. Moreover, there is no simple way of predicting these values, or even of explaining the trends that are observed for the solubilities of different anions within a given group of the periodic table.



Ultimately, the driving force for dissolution (and for *all* chemical processes) is determined by the Gibbs free energy change. Dissolution of a salt is conceptually understood as a sequence of the two processes depicted above:

1. breakup of the ionic lattice of the solid (i.e., lattice energy)
2. followed by attachment of water molecules to the released ions (Solvation or Hydration Energy).

The first step consumes a large quantity of energy, something that by itself would strongly discourage solubility. But the second step *releases* a large amount of energy and thus has the opposite effect. Thus the net energy change depends on the sum of two large energy terms (often approaching 1000 kJ/mol) having opposite signs. Each of these terms will to some extent be influenced by the size, charge, and polarizability of the particular ions involved, and on the lattice structure of the solid. This large number of variables makes it impossible to predict the solubility of a given salt.

Nevertheless, there are some clear trends for how the solubilities of a series of salts of a given anion (such as hydroxides, sulfates, etc.) change with a periodic table group. And of course, there are a number of general *solubility rules*.

Solubility Rules

1. Salts containing Group I elements are soluble (Li^+, Na^+, K^+, Cs^+, Rb^+). Exceptions to this rule are rare. Salts containing the ammonium ion (NH_4^+) are also soluble.
2. Salts containing nitrate ion (NO_3^-) are generally soluble.
3. Salts containing Cl^-, Br^-, I^- are generally soluble. Important exceptions to this rule are halide salts of Ag^+, Pb^{2+}, and $(Hg_2)^{2+}$. Thus, AgCl, $PbBr_2$, and Hg_2Cl_2 are all insoluble.
4. Most silver salts are insoluble. $AgNO_3$ and $Ag(C_2H_3O_2)$ are common soluble salts of silver; virtually anything else is insoluble.
5. Most sulfate salts are soluble. Important exceptions to this rule include $BaSO_4$, $PbSO_4$, Ag_2SO_4 and $SrSO_4$.
6. Most hydroxide salts are only slightly soluble. Hydroxide salts of Group I elements are soluble. Hydroxide salts of Group II elements (Ca, Sr, and Ba) are slightly soluble. Hydroxide salts of transition metals and Al^{3+} are insoluble. Thus, $Fe(OH)_3$, $Al(OH)_3$, $Co(OH)_2$ are not soluble.
7. Most sulfides of transition metals are highly insoluble. Thus, CdS, FeS, ZnS, Ag_2S are all insoluble. Arsenic, antimony, bismuth, and lead sulfides are also insoluble.
8. Carbonates are frequently insoluble. Group II carbonates (Ca, Sr, and Ba) are insoluble. Some other insoluble carbonates include $FeCO_3$ and $PbCO_3$.
9. Chromates are frequently insoluble. Examples: $PbCrO_4$, $BaCrO_4$
10. Phosphates are frequently insoluble. Examples: $Ca_3(PO_4)_2$, Ag_3PO_4
11. Fluorides are frequently insoluble. Examples: BaF_2, MgF_2 PbF_2.

A solution must be saturated to be in equilibrium with the solid. This is a *necessary* condition for solubility equilibrium, but it is not by itself *sufficient*. True chemical equilibrium can only occur when all components are simultaneously present. A solubility system can be in equilibrium only when some of the solid is in contact with a saturated solution of its ions. Failure to appreciate this is a very common cause of errors in solving solubility problems.

Undersaturated and supersaturated solutions

If the ion product is smaller than the solubility product, the system is not in equilibrium and no solid can be present. Such a solution is said to be *undersaturated*. A *supersaturated* solution is one in which the ion product exceeds the solubility product. A supersaturated solution is not at equilibrium, and no solid can ordinarily be present in such a solution. If some of the solid is added, the excess ions precipitate out and until solubility equilibrium is achieved.

Solubility and Temperature

Solubility usually increases with temperature - but not always. This is very apparent from the solubility-vs.-temperature plots shown in Figure 7.1.1. (Some of the plots are colored differently in order to make it easier to distinguish them where they crowd together.) The temperature dependence of any process depends on its entropy change — that is, on the degree to which thermal kinetic energy can spread throughout the system. When a solid dissolves, its component molecules or ions diffuse into the much greater volume of the solution, carrying their thermal energy along with them. So we would normally expect the entropy to increase — something that makes any process take place to a greater extent at a higher temperature.

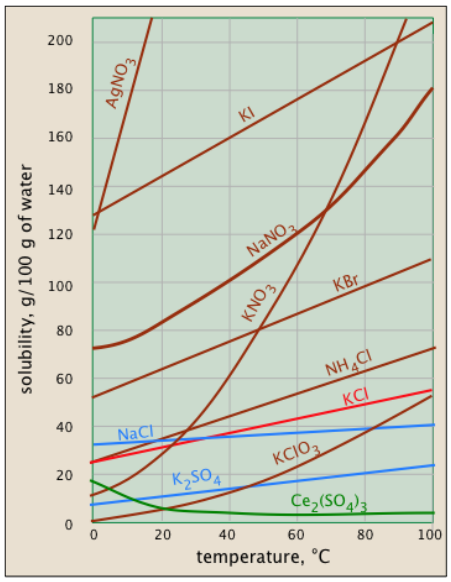


Figure 7.1.1: Solubility of select salts in water as a function of temperature.

So why does the solubility of cerium sulfate (green plot) diminish with temperature? Dispersal of the Ce^{3+} and SO_4^{2-} ions themselves is still associated with an entropy increase, but in this case the entropy of the *water*decreases even more owing to the ordering of the H_2O molecules that attach to the Ce^{3+} ions as they become hydrated. It's difficult to predict these effects, or explain why they occur in individual cases — but they do happen.

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7.2: Ionic Equilibria between Solids and Solutions

Learning Objectives

- To calculate the solubility of an ionic compound from its K_{sp}

We begin our discussion of solubility and complexation equilibria—those associated with the formation of complex ions—by developing quantitative methods for describing dissolution and precipitation reactions of ionic compounds in aqueous solution. Just as with acid–base equilibria, we can describe the concentrations of ions in equilibrium with an ionic solid using an equilibrium constant expression.

The Solubility Product

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:



As you will discover in more advanced chemistry courses, basic anions, such as S^{2-}, PO_4^{3-}, and CO_3^{2-}, react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate.

The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore



At 25°C and pH 7.00, Ksp for calcium phosphate is 2.07×10^{-33}, indicating that the concentrations of Ca^{2+} and PO_4^{3-} ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts are listed in Table 7.2.1, which shows that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH in Equations 1.1.3 and 1.2.8, changes in pH can affect the solubility of a compound as discussed later.

> As with K, the concentration of a pure solid does not appear explicitly in K_{sp}.

Table 7.2.1: Solubility Products for Selected Ionic Substances at 25°C

Solid	Color	Ksp	Solid	Color	Ksp
Acetates			**Iodides**		
$Ca(O_2CCH_3)_2{\cdot}3H_2O$	white	4×10^{-3}	Hg_2I_2*	yellow	5.2×10^{-29}
Bromides			PbI_2	yellow	9.8×10^{-9}
AgBr	off-white	5.35×10^{-13}	**Oxalates**		
Hg_2Br_2*	yellow	6.40×10^{-23}	$Ag_2C_2O_4$	white	5.40×10^{-12}
***These contain the Hg_2^{2+} ion.**					

Solid	Color	Ksp	Solid	Color	Ksp
Carbonates			$MgC_2O_4 \cdot 2H_2O$	white	4.83×10^{-6}
$CaCO_3$	white	3.36×10^{-9}	PbC_2O_4	white	4.8×10^{-10}
$PbCO_3$	white	7.40×10^{-14}	**Phosphates**		
Chlorides			Ag_3PO_4	white	8.89×10^{-17}
AgCl	white	1.77×10^{-10}	$Sr_3(PO_4)_2$	white	4.0×10^{-28}
Hg_2Cl_2*	white	1.43×10^{-18}	$FePO_4 \cdot 2H_2O$	pink	9.91×10^{-16}
$PbCl_2$	white	1.70×10^{-5}	**Sulfates**		
Chromates			Ag_2SO_4	white	1.20×10^{-5}
$CaCrO_4$	yellow	7.1×10^{-4}	$BaSO_4$	white	1.08×10^{-10}
$PbCrO_4$	yellow	2.8×10^{-13}	$PbSO_4$	white	2.53×10^{-8}
Fluorides			**Sulfides**		
BaF_2	white	1.84×10^{-7}	Ag_2S	black	6.3×10^{-50}
PbF_2	white	3.3×10^{-8}	CdS	yellow	8.0×10^{-27}
Hydroxides			PbS	black	8.0×10^{-28}
$Ca(OH)_2$	white	5.02×10^{-6}	ZnS	white	1.6×10^{-24}
$Cu(OH)_2$	pale blue	1×10^{-14}			
$Mn(OH)_2$	light pink	1.9×10^{-13}			
$Cr(OH)_3$	gray-green	6.3×10^{-31}			
$Fe(OH)_3$	rust red	2.79×10^{-39}			

***These contain the Hg_2^{2+} ion.**

Solubility products are determined experimentally by directly measuring either the concentration of one of the component ions or the solubility of the compound in a given amount of water. However, whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp}, like K, is defined in terms of the molar concentrations of the component ions.



A color photograph of a kidney stone, 8 mm in length. Kidney stones form from sparingly soluble calcium salts and are largely composed of $Ca(O_2CCO_2)·H_2O$ and $Ca_3(PO_4)_2$. from Wikipedia.

Example 7.2.1: Kidney Stones

Calcium oxalate monohydrate [$Ca(O_2CCO_2)·H_2O$, also written as $CaC_2O_4·H_2O$] is a sparingly soluble salt that is the other major component of kidney stones [along with $Ca_3(PO_4)_2$]. Its solubility in water at 25°C is 7.36×10^{-4} g/100 mL. Calculate its K_{sp}.

Given: solubility in g/100 mL

Asked for: K_{sp}

Strategy:

A. Write the balanced dissolution equilibrium and the corresponding solubility product expression.
B. Convert the solubility of the salt to moles per liter. From the balanced dissolution equilibrium, determine the equilibrium concentrations of the dissolved solute ions. Substitute these values into the solubility product expression to calculate K_{sp}.

Solution

A We need to write the solubility product expression in terms of the concentrations of the component ions. For calcium oxalate monohydrate, the balanced dissolution equilibrium and the solubility product expression (abbreviating oxalate as ox^{2-}) are as follows:

$$\mathrm{Ca(O_2CCO_2)\cdot H_2O(s) \rightleftharpoons Ca^{2+}(aq) + {^-O_2CCO_2^-}(aq) + H_2O(l)} \qquad K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{ox^{2-}}]$$

Neither solid calcium oxalate monohydrate nor water appears in the solubility product expression because their concentrations are essentially constant.

B Next we need to determine $[Ca^{2+}]$ and $[ox^{2-}]$ at equilibrium. We can use the mass of calcium oxalate monohydrate that dissolves in 100 mL of water to calculate the number of moles that dissolve in 100 mL of water. From this we can determine the number of moles that dissolve in 1.00 L of water. For dilute solutions, the density

of the solution is nearly the same as that of water, so dissolving the salt in 1.00 L of water gives essentially 1.00 L of solution. Because each 1 mol of dissolved calcium oxalate monohydrate dissociates to produce 1 mol of calcium ions and 1 mol of oxalate ions, we can obtain the equilibrium concentrations that must be inserted into the solubility product expression. The number of moles of calcium oxalate monohydrate that dissolve in 100 mL of water is as follows:

$$\frac{7.36 \times 10^{-4}\ \text{g}}{146.1\ \text{g/mol}} = 5.04 \times 10^{-6}\ \text{mol}\ \text{Ca}(\text{O}_2\text{CCO}_2) \cdot \text{H}_2\text{O}$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$\left(\frac{5.04 \times 10^{-6}\ \text{mol}\ \text{Ca}(\text{O}_2\text{CCO}_2\cdot)\text{H}_2\text{O}}{100\ \text{mL}}\right)\left(\frac{1000\ \text{mL}}{1.00\ \text{L}}\right) = 5.04 \times 10^{-5}\ \text{mol/L} = 5.04 \times 10^{-5}\ \text{M}$$

Because of the stoichiometry of the reaction, the concentration of Ca^{2+} and ox^{2-} ions are both 5.04×10^{-5} M. Inserting these values into the solubility product expression,

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (5.04 \times 10^{-5})(5.04 \times 10^{-5}) = 2.54 \times 10^{-9}$$

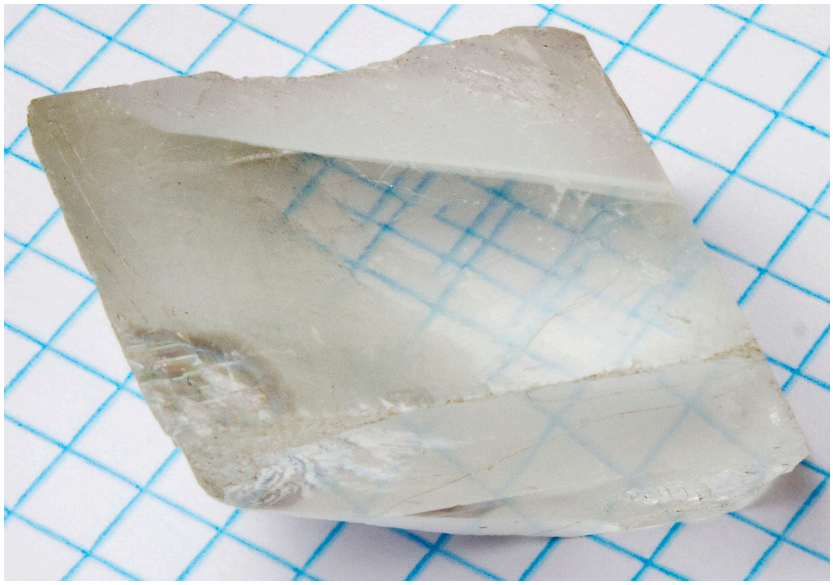
In our calculation, we have ignored the reaction of the weakly basic anion with water, which tends to make the actual solubility of many salts greater than the calculated value.

Exercise 7.2.1

One crystalline form of calcium carbonate ($CaCO_3$) is the mineral sold as “calcite” in mineral and gem shops. The solubility of calcite in water is 0.67 mg/100 mL. Calculate its K_{sp}.

Answer 4.5×10^{-9}

The reaction of weakly basic anions with H_2O tends to make the actual solubility of many salts higher than predicted.



A crystal of calcite ($CaCO_3$), illustrating the phenomenon of double refraction. When a transparent crystal of calcite is placed over a page, we see two images of the letters. Image used with permisison from Wikipedia

Calcite, a structural material for many organisms, is found in the teeth of sea urchins. The urchins create depressions in limestone that they can settle in by grinding the rock with their teeth. Limestone, however, also consists of calcite, so how can the urchins

grind the rock without also grinding their teeth? Researchers have discovered that the teeth are shaped like needles and plates and contain magnesium. The concentration of magnesium increases toward the tip, which contributes to the hardness. Moreover, each tooth is composed of two blocks of the polycrystalline calcite matrix that are interleaved near the tip. This creates a corrugated surface that presumably increases grinding efficiency. Toolmakers are particularly interested in this approach to grinding.

Tabulated values of K_{sp} can also be used to estimate the solubility of a salt with a procedure that is essentially the reverse of the one used in Example 7.2.1. In this case, we treat the problem as a typical equilibrium problem and set up a table of initial concentrations, changes in concentration, and final concentrations (ICE Tables), remembering that the concentration of the pure solid is essentially constant.

Example 7.2.2

We saw that the K_{sp} for $Ca_3(PO_4)_2$ is 2.07×10^{-33} at 25°C. Calculate the aqueous solubility of $Ca_3(PO_4)_2$ in terms of the following:

a. the molarity of ions produced in solution
b. the mass of salt that dissolves in 100 mL of water at 25°C

Given: K_{sp}

Asked for: molar concentration and mass of salt that dissolves in 100 mL of water

Strategy:

A. Write the balanced equilibrium equation for the dissolution reaction and construct a table showing the concentrations of the species produced in solution. Insert the appropriate values into the solubility product expression and calculate the molar solubility at 25°C.
B. Calculate the mass of solute in 100 mL of solution from the molar solubility of the salt. Assume that the volume of the solution is the same as the volume of the solvent.

Solution:

A. **A** The dissolution equilibrium for $Ca_3(PO_4)_2$ (Equation 1.1.3) is shown in the following ICE table. Because we are starting with distilled water, the initial concentration of both calcium and phosphate ions is zero. For every 1 mol of $Ca_3(PO_4)_2$ that dissolves, 3 mol of Ca^{2+} and 2 mol of PO_4^{3-} ions are produced in solution. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ will be $+3x$, and the change in $[PO_4^{3-}]$ will be $+2x$. We can insert these values into the table.

$$\mathbf{Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)}$$

	$Ca_3(PO_4)_2$	$[Ca^{2+}]$	$[PO_4^{3-}]$
initial	pure solid	0	0
change	—	$+3x$	$+2x$
final	pure solid	$3x$	$2x$

Although the amount of solid $Ca_3(PO_4)_2$ changes as some of it dissolves, its molar concentration does not change. We now insert the expressions for the equilibrium concentrations of the ions into the solubility product expression (Equation 17.2):

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3x)^3(2x)^2$$
$$2.07 \times 10^{-33} = 108x^5$$
$$1.92 \times 10^{-35} = x^5$$
$$1.14 \times 10^{-7}\ M = x$$

This is the molar solubility of calcium phosphate at 25°C. However, the molarity of the ions is 2*x* and 3*x*, which means that $[PO_4^{3-}] = 2.28 \times 10^{-7}$ and $[Ca^{2+}] = 3.42 \times 10^{-7}$.

b. **B** To find the mass of solute in 100 mL of solution, we assume that the density of this dilute solution is the same as the density of water because of the low solubility of the salt, so that 100 mL of water gives 100 mL of solution. We can then determine the amount of salt that dissolves in 100 mL of water:

$$\left(\frac{1.14 \times 10^{-7}\ \text{mol}}{1\ \text{L}}\right) 100\ \text{mL} \left(\frac{1\ \text{L}}{1000\ \text{mL}}\right) \left(\frac{310.18\ \text{g}\ Ca_3(PO_4)_2}{1\ \text{mol}}\right) = 3.54 \times 10^{-6}\ \text{g}\ Ca_3(PO_4)_2$$

Exercise 7.2.2

The solubility product of silver carbonate (Ag_2CO_3) is 8.46×10^{-12} at 25°C. Calculate the following:

a. the molarity of a saturated solution
b. the mass of silver carbonate that will dissolve in 100 mL of water at this temperature

Answer a

1.28×10^{-4} M

Answer a

3.54 mg

Relating Solubilities to Solubility Constants

The *solubility* (by which we usually mean the *molar solubility*) of a solid is expressed as the concentration of the "dissolved solid" in a *saturated solution*. In the case of a simple 1:1 solid such as AgCl, this would just be the concentration of Ag^+ or Cl^- in the saturated solution. But for a more complicated stoichiometry such as as silver chromate, the solubility would be only one-half of the Ag^+ concentration.

For example, let us denote the solubility of Ag_2CrO_4 as S mol L^{-1}. Then for a saturated solution, we have

- $[Ag^+] = 2S$
- $[CrO_4^{2-}] = S$

Substituting this into Eq 5b above,

$$(2S)^2(S) = 4S^3 = 2.76 \times 10^{-12} \qquad (7.2.1651)$$

[redacted]

thus the solubility is $8.8 \times 10^{-5}\ \ M$.

Note that the relation between the solubility and the solubility product constant depends on the stoichiometry of the dissolution reaction. For this reason it is meaningless to compare the solubilities of two salts having the formulas A_2B and AB_2, say, on the basis of their K_s values.

It is *meaningless* to compare the solubilities of two salts having different formulas on the basis of their K_s values.

Example 7.2.2

The solubility of CaF_2 (molar mass 78.1) at 18°C is reported to be 1.6 mg per 100 mL of water. Calculate the value of K_s under these conditions.

Solution

moles of solute in 100 mL; S = 0.0016 g / 78.1 g/mol = 2.05×10^{-5} mol

$$S = \frac{2.05 \times 10^{-5} mol}{0.100\ L}$$
$$= 2.05 \times 10^{-4} M$$

$$K_{sp} = [Ca^{2+}][F^-]^2$$
$$= (S)(2S)^2$$
$$= 4 \times (2.05 \times 10^{-4})^3$$
$$= 3.44 \times 10^{-11}$$

Example 7.2.3

Estimate the solubility of $La(IO_3)_3$ and calculate the concentration of iodate in equilibrium with solid lanthanum iodate, for which $K_s = 6.2 \times 10^{-12}$.

Solution

The equation for the dissolution is

$$\mathrm{La(IO_3)_3 \rightleftharpoons La^{3+} + 3\,IO_3^-}$$

If the solubility is S, then the equilibrium concentrations of the ions will be

$[La^{3+}] = S$ and $[IO_3^-] = 3S$. Then $K_s = [La^{3+}][IO_3^-]^3 = S(3S)^3 = 27S^4$

$27S^4 = 6.2 \times 10^{-12}$, $S = ((6.2 \div 27) \times 10^{-12})^{¼} = 6.92 \times 10^{-4}$ *M*

$[IO_3^-] = 3S = 2.08 \times 10^{-5}$ (*M*)

Example 7.2.4: Cadmium

Cadmium is a highly toxic environmental pollutant that enters wastewaters associated with zinc smelting (Cd and Zn commonly occur together in ZnS ores) and in some electroplating processes. One way of controlling cadmium in effluent streams is to add sodium hydroxide, which precipitates insoluble $Cd(OH)_2$ (K_s = 2.5E–14). If 1000 L of a certain wastewater contains Cd^{2+} at a concentration of 1.6E–5 *M*, what concentration of Cd^{2+} would remain after addition of 10 L of 4 *M* NaOH solution?

Solution

As with most real-world problems, this is best approached as a series of smaller problems, making simplifying approximations as appropriate.

Volume of treated water: 1000 L + 10 L = 1010 L

Concentration of OH^- on addition to 1000 L of pure water:

$$(4\ M) \times (10\ L)/(1010\ L) = 0.040\ M$$

Initial concentration of Cd^{2+} in 1010 L of water:

$$(1.6 \times 10^{-5}\ M)\left(\frac{100}{101}\right) \approx 1.6 \times 10^{-5}\ M \tag{7.2.1652}$$

The easiest way to tackle this is to start by assuming that a stoichiometric quantity of $Cd(OH)_2$ is formed — that is, *all* of the Cd^{2+} gets precipitated.

Concentrations	$[Cd^{2+}]$, *M*	$[OH^-]$, *M*
initial	1.6E–5	0.04
change	–1.6E–5	–3.2E–5
final:	0	0.04 – 3.2E–5 ≈ .04

Now "turn on the equilibrium" — find the concentration of Cd^{2+} that can exist in a 0.04*M* OH^- solution:

Concentrations	$[Cd^{2+}]$, *M*	$[OH^-]$, *M*
initial	o	0.04
change	+*x*	+2*x*
at equilibrium	*x*	.04 + 2*x* ≈ .04

Substitute these values into the solubility product expression:

$$Cd(OH)_2(s) = [Cd^{2+}]\ [OH^-]^2 = 2.5E{-}14$$

$$[Cd^{2+}] = (2.5E{-}14)\ /\ (16E{-}4) = 1.6E{-}13\ M$$

Note that the effluent will now be very alkaline:

$$pH = 14 + log 0.04 = 12.6 \tag{7.2.1653}$$

so in order to meet environmental standards an equivalent quantity of strong acid must be added to neutralize the water before it is released.

Summary

The solubility product (K_{sp}) is used to calculate equilibrium concentrations of the ions in solution, whereas the ion product (Q) describes concentrations that are not necessarily at equilibrium. The equilibrium constant for a dissolution reaction, called the solubility product (K_{sp}), is a measure of the solubility of a compound. Whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp} is defined in terms of the molar concentrations of the component ions.

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7.3: Precipitation and the Solubility Product

Learning Objectives

- Define K_{sp}, the solubility product.
- Explain solid/solution equilibria using K_{sp} and Q_{sp}.
- Calculate molarity of saturated solution from K_{sp}.
- Calculate K_{sp} from molarity of saturated solution.

Precipitation reactions occur when cations and anions in aqueous solution combine to form an insoluble ionic solid called a **precipitate**. Whether or not such a reaction occurs can be determined by using the **solubility rules** for common ionic solids. Because not all aqueous reactions form precipitates, one must consult the solubility rules before determining the state of the products and writing a **net ionic equation.** The ability to predict these reactions allows scientists to determine which ions are present in a solution, and allows industries to form chemicals by extracting components from these reactions.

Properties of Precipitates

Precipitates are insoluble ionic solid products of a reaction, formed when certain cations and anions combine in an aqueous solution. The determining factors of the formation of a precipitate can vary. Some reactions depend on temperature, such as solutions used for buffers, whereas others are dependent only on solution concentration. The solids produced in precipitate reactions are crystalline solids, and can be suspended throughout the liquid or fall to the bottom of the solution. The remaining fluid is called **supernatant liquid** (or just the supernate). The two components of the mixture (precipitate and supernate) can be separated by various methods, such as filtration, centrifuging, or decanting.

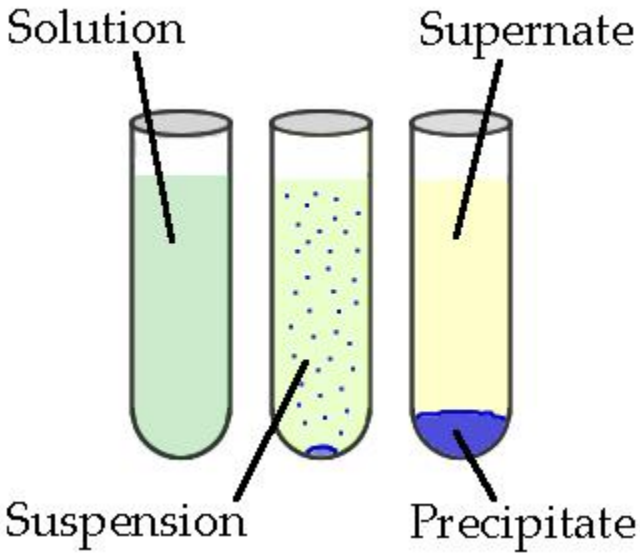


Figure 7.3.1: Above is a diagram of the formation of a precipitate in solution. (Public Domain; ZabMilenko)

The use of solubility rules require an understanding of the way that ions react. Most precipitation reactions are single replacement reactions or double replacement reactions. A double replacement reaction occurs when two ionic reactants dissociate and bond with the respective anion or cation from the other reactant. The ions replace each other based on their charges as either a cation or an anion. This can be thought of as a double displacement reaction where the partners "switching; that is, the two reactants each "lose" their partner and form a bond with a different partner:

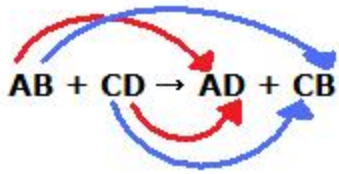


Figure 7.3.2: A double replacement reaction

A double replacement reaction is specifically classified as a **precipitation reaction** when the chemical equation in question occurs in aqueous solution and one of the of the products formed is insoluble. An example of a precipitation reaction is given below:

$$\mathrm{CdSO_4\,(aq) + K_2S\,(aq)\ \rightarrow CdS\,(s) + K_2SO_4\,(aq)} \tag{7.3.1654}$$

Both reactants are aqueous and one product is solid. Because the reactants are ionic and aqueous, they dissociate and are therefore **soluble**. However, there are six solubility guidelines used to predict which molecules are insoluble in water. These molecules form a solid precipitate in solution.

Solubility Rules

Whether or not a reaction forms a precipitate is dictated by the solubility rules. These rules provide guidelines that tell which ions form solids and which remain in their ionic form in aqueous solution. The rules are to be followed from the top down, meaning that if something is insoluble (or soluble) due to rule 1, it has precedence over a higher-numbered rule.

1. Salts formed with group 1 cations and $\mathrm{NH_4^+}$ cations are **soluble**. There are some exceptions for certain Li^+ salts.
2. Acetates ($\mathrm{C_2H_3O_2^-}$), nitrates ($\mathrm{NO_3^-}$), and perchlorates ($\mathrm{ClO_4^-}$) are **soluble.**
3. Bromides, chlorides, and iodides are **soluble.**
4. Sulfates ($\mathrm{SO_4^{2-}}$) are **soluble** with the exception of sulfates formed with $\mathrm{Ca^{2+}}$, $\mathrm{Sr^{2+}}$, and $\mathrm{Ba^{2+}}$.
5. Salts containing silver, lead, and mercury (I) are **insoluble.**
6. Carbonates ($\mathrm{CO_3^{2-}}$), phosphates ($\mathrm{PO_4^{3-}}$), sulfides, oxides, and hydroxides ($\mathrm{OH^-}$) are **insoluble**. Sulfides formed with group 2 cations and hydroxides formed with calcium, strontium, and barium are exceptions.

If the rules state that an ion is soluble, then it remains in its aqueous ion form. If an ion is insoluble based on the solubility rules, then it forms a solid with an ion from the other reactant. If all the ions in a reaction are shown to be soluble, then no precipitation reaction occurs.

Net Ionic Equations

To understand the definition of a **net ionic equation**, recall the equation for the double replacement reaction. Because this particular reaction is a precipitation reaction, states of matter can be assigned to each variable pair:

$$AB(aq) + CD(aq) \rightarrow AD(aq) + CB(s) \tag{7.3.1655}$$

The first step to writing a net ionic equation is to separate the soluble (aqueous) reactants and products into their respective cations and anions. Precipitates do not dissociate in water, so the solid should not be separated. The resulting equation looks like that below:

$$A^+(aq) + B^-(aq) + C^+(aq) + D^-(aq) \rightarrow A^+(aq) + D^-(aq) + CB(s) \tag{7.3.1656}$$

In the equation above, **A^+** and **D^-** ions are present on both sides of the equation. These are called **spectator ions** because they remain unchanged throughout the reaction. Since they go through the equation unchanged, they can be eliminated to show the **net ionic equation**:

$$B^-(aq) + C^+(aq) \rightarrow +CB(s) \tag{7.3.1657}$$

The net ionic equation only shows the precipitation reaction. A net ionic equation must be balanced on both sides not only in terms of atoms of elements, but also in terms of electric charge. Precipitation reactions are usually represented solely by net ionic equations. If all products are aqueous, a net ionic equation cannot be written because all ions are canceled out as spectator ions. Therefore, **no precipitation reaction occurs**

Equilibrium and non-Equilibrium Conditions

The **ion product (Q)** of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (Q) discussed for gaseous equilibria. Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are not necessarily equilibrium concentrations. An ion product can in principle have *any* positive value, depending on the concentrations of the ions involved. Only in the special case when its value is identical with K_s does it become the solubility product. A solution in which this is the case is said to be *saturated*. Thus when

$$[\mathrm{Ag^+}]^2\,[\mathrm{CrO_4}^{2-}] = 2.76 \times 10^{-12} \tag{7.3.1658}$$

at the temperature and pressure at which this value K_{sp} of applies, we say that the "solution is saturated in silver chromate".

> The ion product Q is analogous to the reaction quotient Q for gaseous equilibria.

As summarized in Figure 7.3.3, there are three possible conditions for an aqueous solution of an ionic solid:

- $Q < K_{sp}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
- $Q = K_{sp}$. The solution is saturated and at equilibrium.
- $Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

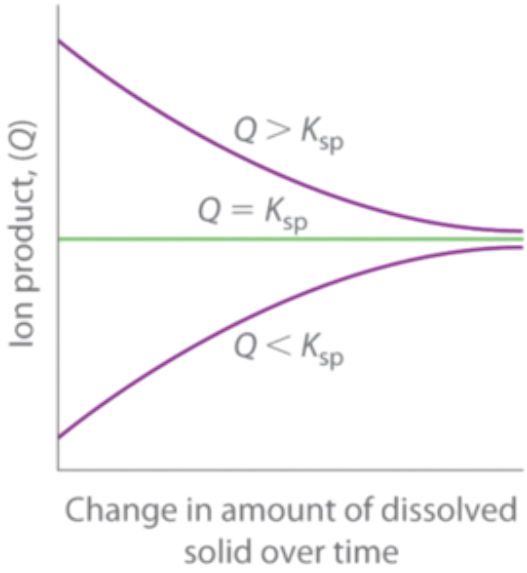


Figure 7.3.3: The Relationship between Q and K_{sp}. If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium (Q = K_{sp}). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until Q = K_{sp}. If Q = K_{sp}, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur. (CC BY-SA-NC; Anonymous)

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

Example 7.3.3: barium milkshakes

Barium sulfate is used in medical imaging of the gastrointestinal tract. Its solubility product is 1.08×10^{-10} at 25°C, so it is ideally suited for this purpose because of its low solubility when a "barium milkshake" is consumed by a patient. The pathway of the sparingly soluble salt can be easily monitored by x-rays. Will barium sulfate precipitate if 10.0 mL of 0.0020 M Na_2SO_4 is added to 100 mL of 3.2×10^{-4} M $BaCl_2$? Recall that NaCl is highly soluble in water.

Given: K_{sp} and volumes and concentrations of reactants

Asked for: whether precipitate will form

Strategy:

A. Write the balanced equilibrium equation for the precipitation reaction and the expression for K_{sp}.
B. Determine the concentrations of all ions in solution when the solutions are mixed and use them to calculate the ion product (Q).
C. Compare the values of Q and K_{sp} to decide whether a precipitate will form.

Solution

A The only slightly soluble salt that can be formed when these two solutions are mixed is $\mathrm{BaSO_4}$ because NaCl is highly soluble. The equation for the precipitation of $\mathrm{BaSO_4}$ is as follows:

$$\mathrm{BaSO_4\,(s) \rightleftharpoons Ba^{2+}\,(aq) + SO_4^{2-}\,(aq)}$$

The solubility product expression is as follows:

$$K_{sp} = [\mathrm{Ba^{2+}}][\mathrm{SO_4}^{2-}] = 1.08 \times 10^{-10}$$

B To solve this problem, we must first calculate the ion product:

$$Q = [\mathrm{Ba^{2+}}][\mathrm{SO_4}^{2-}]$$

using the concentrations of the ions that are present after the solutions are mixed and before any reaction occurs. The concentration of Ba^{2+} when the solutions are mixed is the total number of moles of Ba^{2+} in the original 100 mL of $\mathrm{BaCl_2}$ solution divided by the final volume (100 mL + 10.0 mL = 110 mL):

$$\text{moles } \mathrm{Ba^{2+}} = 100 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{3.2 \times 10^{-4} \text{ mol}}{1 \text{ L}}\right) = 3.2 \times 10^{-5} \text{ mol } \mathrm{Ba^{2+}}$$

$$[\mathrm{Ba^{2+}}] = \left(\frac{3.2 \times 10^{-5} \text{ mol } \mathrm{Ba^{2+}}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 2.9 \times 10^{-4} \text{ M } \mathrm{Ba^{2+}}$$

Similarly, the concentration of SO_4^{2-} after mixing is the total number of moles of SO_4^{2-} in the original 10.0 mL of Na_2SO_4 solution divided by the final volume (110 mL):

$$\text{moles } \mathrm{SO_4^{2-}} = 10.0 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{0.0020 \text{ mol}}{1 \text{ L}}\right) = 2.0 \times 10^{-5} \text{ mol } \mathrm{SO_4^{2-}}$$

$$[\mathrm{SO_4^{2-}}] = \left(\frac{2.0 \times 10^{-5} \text{ mol } \mathrm{SO_4^{2-}}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 1.8 \times 10^{-4} \text{ M } \mathrm{SO_4^{2-}}$$

We can now calculate \(Q\):

$$Q = [\mathrm{Ba^{2+}}][\mathrm{SO_4}^{2-}] = (2.9 \times 10^{-4})(1.8 \times 10^{-4}) = 5.2 \times 10^{-8}$$

C We now compare Q with the K_{sp}. If Q > K_{sp}, then $\mathrm{BaSO_4}$ will precipitate, but if Q < K_{sp}, it will not. Because Q > K_{sp}, we predict that $\mathrm{BaSO_4}$ will precipitate when the two solutions are mixed. In fact, $\mathrm{BaSO_4}$ will continue to precipitate until the system reaches equilibrium, which occurs when

$$[\mathrm{Ba^{2+}}][\mathrm{SO_4^{2-}}] = K_{sp} = 1.08 \times 10^{-10}.$$

Exercise 7.3.3

The solubility product of calcium fluoride ($\mathrm{CaF_2}$) is 3.45×10^{-11}. If 2.0 mL of a 0.10 M solution of NaF is added to 128 mL of a $2.0 \times 10^{-5}\ M$ solution of $\mathrm{Ca(NO_3)_2}$, will $\mathrm{CaF_2}$ precipitate?

Answer

Yes, since $Q_{sp} = 4.7 \times 10^{-11} > K_{sp}$.

A solution must be saturated to be in equilibrium with the solid. This is a *necessary* condition for solubility equilibrium, but it is not by itself *sufficient*. True chemical equilibrium can only occur when all components are simultaneously present. A solubility system can be in equilibrium only when some of the solid is in contact with a saturated solution of its ions. Failure to appreciate this is a very common cause of errors in solving solubility problems.

Undersaturated and supersaturated solutions

If the ion product is smaller than the solubility product, the system is not in equilibrium and no solid can be present. Such a solution is said to be *undersaturated*. A *supersaturated* solution is one in which the ion product exceeds the solubility product. A supersaturated solution is not at equilibrium, and no solid can ordinarily be present in such a solution. If some of the solid is added, the excess ions precipitate out and until solubility equilibrium is achieved.

How to know the saturation status of a solution? Just comparing the ion product Q_s with the solubility product K_{sp}. as shown in Table 7.3.1.

Table 7.3.1: relationship among Q_{sp}, K_{sp} and saturation

Q_{sp}/K_{sp}	Status
> 1	Product concentration too high for equilibrium; net reaction proceeds to **left**.
= 1	System is at equilibrium; **no net change** will occur.
< 1	Product concentration too low for equilibrium; net reaction proceeds to **right**.

For example, for the system



a solution in which $Q_s < K_s$ (i.e., $K_s / Q_s > 1$) is undersaturated (blue shading) and the no solid will be present. The combinations of $[Ag^+]$ and $[CrO_4^{2-}]$ that correspond to a saturated solution (and thus to equilibrium) are limited to those described by the curved line. The pink area to the right of this curve represents a supersaturated solution.

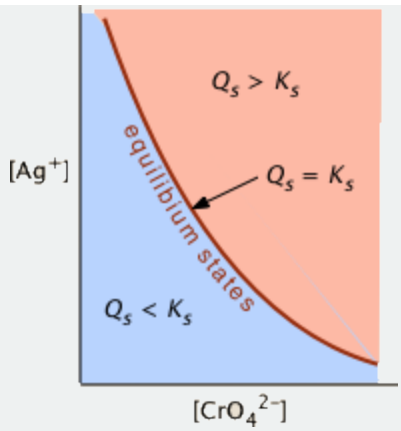


Figure 7.3.4: Equilibrium vs. non-equilibrium states for $\mathrm{Ag_2CrO_4\,(s)}$. (CC BY; Stephen Lower).

For some substances, formation of a solid or crystallization does not occur automatically whenever a solution is saturated. These substances have a tendency to form oversaturated solutions. For example, syrup and honey are oversaturated sugar solutions, containing other substances such as citric acids. For oversatureated solutions, Q_{sp} is greater than K_{sp}. When a seed crystal is provided or formed, a precipitate will form immediately due to equilibrium of requiring Q_{sp} to approach K_{sp}. For example Sodium acetate trihydrate, $\mathrm{NaCH_3COO \cdot 3\,H_2O}$, when heated to 370 K will become a liquid and stays as a liquid when cooled to room temperature or even below 273 K (Video 7.3.1). As soon as a seed crystal is present, crystallization occurs rapidly. In such a process, heat is released since this is an exothermic process $\Delta H < 0$.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

https://www.youtube.com/embed/BLq5NibwV5g?vq=hd1080

Video 7.3.1***:*** *"hot ice" (sodium acetate) crystallized from a non-equilibrium supersaturated ($Q_{sp} > K_{sp}$) solution*

Example 7.3.1

A sample of groundwater that has percolated through a layer of gypsum ($CaSO_4$) with $K_{sp} = 4.9 \times 10^{-5} = 10^{-4.3}$) is found to have be $8.4 \times 10^{-5}\ \ M$ in Ca^{2+} and $7.2 \times 10^{-5}\ \ M$ in SO_4^{2-}. What is the equilibrium state of this solution with respect to gypsum?

Solution

The ion product

$$Q_s = (8.4 \times 10^{-5})(7.2 \times 10^{-5}) = 6.0 \times 10^{-4}$$

exceeds K_{sp}, so the ratio $K_{sp}\ /Q_{sp} > 1$ and the solution is *supersaturated* in $CaSO_4$.

Relating Solubilities to Solubility Constants

The *solubility* (by which we usually mean the *molar solubility*) of a solid is expressed as the concentration of the "dissolved solid" in a *saturated solution*. In the case of a simple 1:1 solid such as AgCl, this would just be the concentration of Ag^+ or Cl^- in the saturated solution. But for a more complicated stoichiometry such as as silver chromate, the solubility would be only one-half of the Ag^+ concentration.

For example, let us denote the solubility of Ag_2CrO_4 as S mol L^{-1}. Then for a saturated solution, we have

- $[Ag^+] = 2S$
- $[CrO_4^{2-}] = S$

Substituting this into Eq 5b above,

$$(2S)^2(S) = 4S^3 = 2.76 \times 10^{-12} \tag{7.3.1659}$$

thus the solubility is $8.8 \times 10^{-5}\ \ M$.

Note that the relation between the solubility and the solubility product constant depends on the stoichiometry of the dissolution reaction. For this reason it is meaningless to compare the solubilities of two salts having the formulas A_2B and AB_2, say, on the basis of their K_s values.

> It is *meaningless* to compare the solubilities of two salts having different formulas on the basis of their K_s values.

Example 7.3.2

The solubility of CaF_2 (molar mass 78.1) at 18°C is reported to be 1.6 mg per 100 mL of water. Calculate the value of K_s under these conditions.

Solution

moles of solute in 100 mL; S = 0.0016 g / 78.1 g/mol = 2.05×10^{-5} mol

$$S = \frac{2.05 \times 10^{-5} mol}{0.100\ L} = 2.05 \times 10^{-4} M \tag{7.3.1660}$$

$$K_{sp} = [Ca^{2+}][F^-]^2 = (S)(2S)^2 = 4 \times (2.05 \times 10^{-4})^3 = 3.44 \times 10^{-11} \tag{7.3.1661}$$

Example 7.3.3

Estimate the solubility of $La(IO_3)_3$ and calculate the concentration of iodate in equilibrium with solid lanthanum iodate, for which $K_S = 6.2 \times 10^{-12}$.

Solution

The equation for the dissolution is

$$La(IO_3)_3 \rightleftharpoons La^{3+} + 3IO_3^- \tag{7.3.1662}$$

If the solubility is S, then the equilibrium concentrations of the ions will be

$[La^{3+}] = S$ and $[IO_3^-] = 3S$. Then $K_S = [La^{3+}][IO_3^-]^3 = S(3S)^3 = 27S^4$

$27S^4 = 6.2 \times 10^{-12}$, $S = ((6.2 \div 27) \times 10^{-12})^{¼} = 6.92 \times 10^{-4}$ *M*

$[IO_3^-] = 3S = 2.08 \times 10^{-5}$ (*M*)

Example 7.3.4: Cadmium

Cadmium is a highly toxic environmental pollutant that enters wastewaters associated with zinc smelting (Cd and Zn commonly occur together in ZnS ores) and in some electroplating processes. One way of controlling cadmium in effluent streams is to add sodium hydroxide, which precipitates insoluble $Cd(OH)_2$ (K_S = 2.5E–14). If 1000 L of a certain wastewater contains Cd^{2+} at a concentration of 1.6E–5 *M*, what concentration of Cd^{2+} would remain after addition of 10 L of 4 *M* NaOH solution?

Solution

As with most real-world problems, this is best approached as a series of smaller problems, making simplifying approximations as appropriate.

Volume of treated water: 1000 L + 10 L = 1010 L

Concentration of OH^- on addition to 1000 L of pure water:

(4 *M*) × (10 L)/(1010 L) = 0.040 *M*

Initial concentration of Cd^{2+} in 1010 L of water:

$$(1.6 \times 10^{-5}\ M)\left(\frac{100}{101}\right) \approx 1.6 \times 10^{-5}\ M \tag{7.3.1663}$$

The easiest way to tackle this is to start by assuming that a stoichiometric quantity of $Cd(OH)_2$ is formed — that is, *all* of the Cd^{2+} gets precipitated.

Concentrations	$[Cd^{2+}],\ M$	$[OH^-],\ M$
initial	1.6E–5	0.04
change	–1.6E–5	–3.2E–5
final:	0	0.04 – 3.2E–5 ≈ .04

Now "turn on the equilibrium" — find the concentration of Cd^{2+} that can exist in a 0.04*M* OH^- solution:

Concentrations	$[Cd^{2+}],\ M$	$[OH^-],\ M$
initial	o	0.04
change	+*x*	+2*x*
at equilibrium	*x*	.04 + 2*x* ≈ .04

Substitute these values into the solubility product expression:

$$Cd(OH)_2(s) = [Cd^{2+}]\,[OH^-]^2 = 2.5E{-}14$$

$$[Cd^{2+}] = (2.5E{-}14) / (16E{-}4) = 1.6E{-}13\ M$$

Note that the effluent will now be very alkaline:

$$pH = 14 + \log 0.04 = 12.6 \tag{7.3.1664}$$

so in order to meet environmental standards an equivalent quantity of strong acid must be added to neutralize the water before it is released.

The Common Ion Effect

It has long been known that the solubility of a sparingly soluble ionic substance is markedly decreased in a solution of another ionic compound when the two substances have an ion in common. This is just what would be expected on the basis of the Le Chatelier Principle; whenever the process

[redacted]

is in equilibrium, addition of more fluoride ion (in the form of highly soluble NaF) will shift the composition to the left, reducing the concentration of Ca^{2+}, and thus effectively reducing the solubility of the solid. We can express this quantitatively by noting that the *solubility product expression*

[redacted]

must always hold, even if some of the ionic species involved come from sources other than $CaF_2(s)$. For example, if some quantity *x* of fluoride ion is added to a solution initially in equilibrium with solid CaF_2, we have

- $[Ca^{2+}] = S$
- $[F^-] = 2S + x$

so that

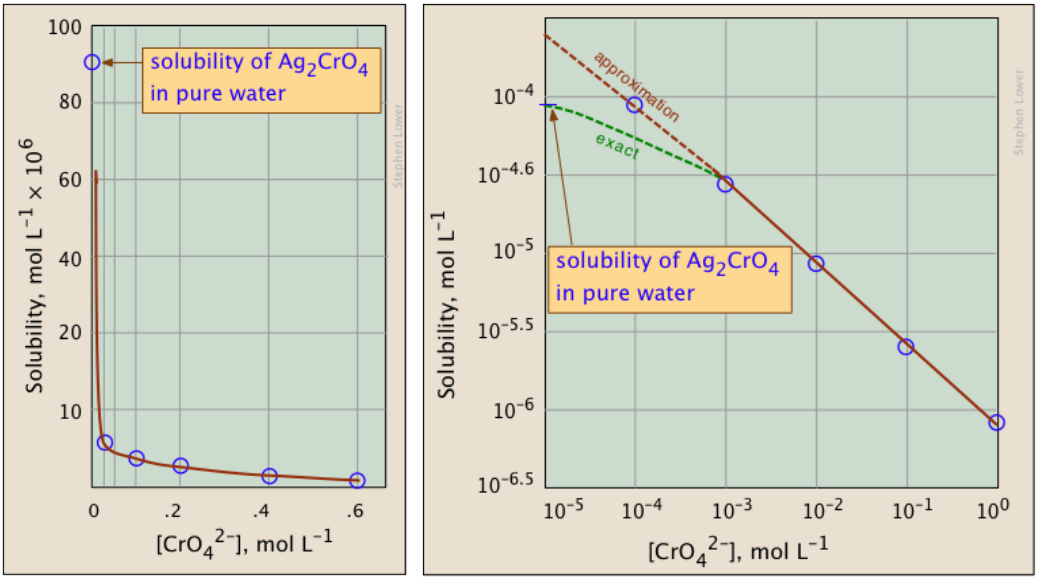
[redacted]

University-level students should be able to derive these relations for ion-derived solids of any stoichiometry. In most practical

cases *x* will be large compared to S so that the 2S term can be dropped and the relation becomes

$$K_{sp} \approx S\,x^2 \tag{7.3.1665}$$

The plots shown below illustrate the common ion effect for silver chromate as the chromate ion concentration is increased by addition of a soluble chromate such as Na_2CrO_4.



What's different about the plot on the right? If you look carefully at the scales, you will see that this one is plotted logarithmically (that is, in powers of 10.) Notice how a much wider a range of values can display on a logarithmic plot. The point of showing this pair of plots is to illustrate the great utility of log-concentration plots in equilibrium calculations in which simple approximations (such as that made in Equation 7.3.1336) can yield straight-lines within the range of values for which the approximation is valid.

Example 7.3.5: strontium sulfate

Calculate the solubility of strontium sulfate (K_s = 2.8 × 10^{-7}) in

a. pure water and
b. in a 0.10 mol L^{-1} solution of Na_2SO_4.

Solution:

(a) In pure water, $K_s = [Sr^{2+}][SO_4^{2-}] = S^2$

$$S = \sqrt{K_s} = (2.8 \times 10^{-7})^{½} = 5.3 \times 10^{-4}$$

(b) In 0.10 mol L^{-1} Na_2SO_4, we have

$$K_s = [Sr^{2+}][SO_4^{2-}] = S \times (0.10 + S) = 2.8 \times 10^{-7}$$

Because S is negligible compared to 0.10 M, we make the approximation

$$K_s = [Sr^{2+}][SO_4^{2-}] \approx S \times (0.10\ M) = 2.8 \times 10^{-7}$$

so S ≈ (2.8 × 10^{-7}) / 0.10M = 2.8 × 10^{-6} *M* — which is roughly 100 times smaller than the result from *(a)*.

Note

The common ion effect usually decreases the solubility of a sparingly soluble salt.

Example 7.3.6

Calculate the solubility of calcium phosphate [$Ca_3(PO_4)_2$] in 0.20 M $CaCl_2$.

Given: concentration of $CaCl_2$ solution

Asked for: solubility of $Ca_3(PO_4)_2$ in $CaCl_2$ solution

Strategy:

A. Write the balanced equilibrium equation for the dissolution of $Ca_3(PO_4)_2$. Tabulate the concentrations of all species produced in solution.
B. Substitute the appropriate values into the expression for the solubility product and calculate the solubility of $Ca_3(PO_4)_2$.

Solution

A The balanced equilibrium equation is given in the following table. If we let *x* equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in [Ca^{2+}] is once again +3*x*, and the change in [$PO_4{}^{3-}$] is +2*x*. We can insert these values into the ICE table.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}(aq) + 2PO^{3-}_{4(aq)} \tag{7.3.1666}$$

	$Ca_3(PO_4)_2$	$[Ca_2{}^+]$	$[PO_{43}{}^-]$
initial	pure solid	0.20	0
change	—	+3*x*	+2*x*
final	pure solid	0.20 + 3*x*	2*x*

B The K_{sp} expression is as follows:

$$K_{sp} = [Ca^{2+}]^3[PO_4{}^{3-}]^2 = (0.20 + 3x)^3(2x)^2 = 2.07\times10^{-33}$$

Because $Ca_3(PO_4)_2$ is a sparingly soluble salt, we can reasonably expect that *x* << 0.20. Thus (0.20 + 3*x*) M is approximately 0.20 M, which simplifies the K_{sp} expression as follows:

$$K_{sp} = (0.20)^3(2x)^2 = 2.07 \times 10^{-33} \tag{7.3.1667}$$
$$x^2 = 6.5 \times 10^{-32} \tag{7.3.1668}$$
$$x = 2.5 \times 10^{-16}\ \text{M} \tag{7.3.1669}$$

This value is the solubility of $Ca_3(PO_4)_2$ in 0.20 M $CaCl_2$ at 25°C. It is approximately nine orders of magnitude less than its solubility in pure water, as we would expect based on Le Chatelier's principle. With one exception, this example is identical to Example 7.3.2—here the initial [Ca^{2+}] was 0.20 M rather than 0.

Exercise 7.3.6

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45×10^{-12} at 25°C.

Answer

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)

Applications and Examples

Precipitation reactions are useful in determining whether a certain element is present in a solution. If a precipitate is formed when a chemical reacts with lead, for example, the presence of lead in water sources could be tested by adding the chemical and monitoring for precipitate formation. In addition, precipitation reactions can be used to extract elements, such as magnesium from seawater. Precipitation reactions even occur in the human body between antibodies and antigens; however, the environment in which this occurs is still being studied.

Example 7.3.7

Complete the double replacement reaction and then reduce it to the net ionic equation.

$$NaOH(aq) + MgCl_{2\ (aq)} \rightarrow$$

First, *predict the products* of this reaction using knowledge of double replacement reactions (remember the cations and anions "switch partners").

$$2NaOH(aq) + MgCl_{2\ (aq)} \rightarrow 2NaCl + Mg(OH)_2$$

Second, *consult the solubility rules* to determine if the products are soluble. Group 1 cations (Na^+) and chlorides are soluble from rules 1 and 3 respectively, so $NaCl$ will be soluble in water. However, rule 6 states that hydroxides are insoluble, and thus $Mg(OH)_2$ will form a precipitate. The resulting equation is the following:

$$2NaOH(aq) + MgCl_{2\ (aq)} \rightarrow 2NaCl(aq) + Mg(OH)_{2\ (s)}$$

Third, *separate the reactants* into their ionic forms, as they would exist in an aqueous solution. Be sure to balance both the electrical charge and the number of atoms:

$$2Na^+(aq) + 2OH^-(aq) + Mg^{2+}(aq) + 2Cl^-(aq) \rightarrow Mg(OH)_{2\ (s)} + 2Na^+(aq) + 2Cl^-(aq)$$

Lastly, *eliminate the spectator ions* (the ions that occur on both sides of the equation unchanged). In this case, they are the sodium and chlorine ions. The final *net ionic equation* is:

$$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_{2(s)}$$

Example 7.3.8

Complete the double replacement reaction and then reduce it to the net ionic equation.

$$CoCl_{2\ (aq)} + Na_2SO_{4\ (aq)} \rightarrow$$

Solution

The predicted products of this reaction are $CoSO_4$ and $NaCl$. From the solubility rules, $CoSO_4$ is soluble because rule 4 states that sulfates (SO_4^{2-}) are soluble. Similarly, we find that $NaCl$ is soluble based on rules 1 and 3. After balancing, the resulting equation is as follows:

$$CoCl_{2\ (aq)} + Na_2SO_{4\ (aq)} \rightarrow CoSO_{4\ (aq)} + 2NaCl(aq)$$

Separate the species into their ionic forms, as they would exist in an aqueous solution. Balance the charge and the atoms. Cancel out all spectator ions (those that appear as ions on both sides of the equation.):

$$\cancel{Co^{2-}}\ (aq) + \cancel{2Cl^-}(aq) + \cancel{2Na^+}\ (aq) + \cancel{SO_4^{2-}}(aq) \rightarrow \cancel{Co^{2-}}\ (aq) + \cancel{SO_4^{2-}}(aq) + \cancel{2Na^+}\ (aq) + \cancel{2Cl^-}(aq)$$

No precipitation reaction

This particular example is important because all of the reactants and the products are aqueous, meaning they cancel out of the net ionic equation. There is no solid precipitate formed; therefore, no precipitation reaction occurs.

Example 7.3.9

Write the net ionic equation for the potentially double displacement reactions. Make sure to include the states of matter and balance the equations.

a. $Fe(NO_3)_{3\ (aq)} + NaOH(aq) \rightarrow$
b. $Al_2(SO_4)_{3\ (aq)} + BaCl_{2\ (aq)} \rightarrow$
c. $HI(aq) + Zn(NO_3)_{2\ (aq)} \rightarrow$
d. $CaCl_{2\ (aq)} + Na_3PO_{4\ (aq)} \rightarrow$
e. $Pb(NO_3)_{2\ (aq)} + K_2SO_{4\ (aq)} \rightarrow$

Solutions

a. Regardless of physical state, the products of this reaction are $Fe(OH)_3$ and $NaNO_3$. The solubility rules predict that $NaNO_3$ is soluble because all nitrates are soluble (rule 2). However, $Fe(OH)_3$ is insoluble, because hydroxides are insoluble (rule 6) and Fe is not one of the cations which results in an exception. After dissociation, the ionic equation is as follows:

$$Fe^{3+}(aq) + NO^-_{3\ (aq)} + Na^+(aq) + 3OH^-(aq) \rightarrow Fe(OH)_{3\ (s)} + Na^+(aq) + NO^-_{3\ (aq)}$$

Canceling out spectator ions leaves the net ionic equation:

$$Fe^{3+}(aq) + OH^-(aq) \rightarrow Fe(OH)_{\ 3(s)}$$

b. From the double replacement reaction, the products are $AlCl_3$ and $BaSO_4$. $AlCl_3$ is soluble because it contains a chloride (rule 3); however, $BaSO_4$ is insoluble: it contains a sulfate, but the Ba^{2+} ion causes it to be insoluble because it is one of the cations that causes an exception to rule 4. The ionic equation is (after balancing):

$$2Al^{3+}(aq) + 6Cl^-(aq) + 3Ba^{2+}(aq) + 3SO^{2-}_{4\ (aq)} \rightarrow 2Al^{3+}(aq) + 6Cl^-(aq) + 3BaSO_{4\ (s)}$$

Canceling out spectator ions leaves the following net ionic equation:

$$Ba^{2+}(aq) + SO^{2-}_{4\ (aq)} \rightarrow BaSO_{4\ (s)}$$

c. From the double replacement reaction, the products HNO_3 and ZnI_2 are formed. Looking at the solubility rules, HNO_3 is soluble because it contains nitrate (rule 2), and ZnI_2 is soluble because iodides are soluble (rule 3). This means that both the products are aqueous (i.e. dissociate in water), and thus no precipitation reaction occurs.

d. The products of this double replacement reaction are $Ca_3(PO_4)_2$ and $NaCl$. Rule 1 states that $NaCl$ is soluble, and according to solubility rule 6, $Ca_3(PO_4)_2$ is insoluble. The ionic equation is:

$$Ca^{2+}(aq) + Cl^{-}(aq) + Na^{+}(aq) + PO^{3-}_{4\ (aq)} \rightarrow Ca_3(PO_4)_{2\ (s)} + Na^{+}(aq) + Cl^{-}(aq)$$

After canceling out spectator ions, the net ionic equation is given below:

$$Ca^{2+}(aq) + PO^{3-}_{4\ (aq)} \rightarrow Ca_3(PO_4)_{2\ (s)}$$

e. The first product of this reaction, $PbSO_4$, is soluble according to rule 4 because it is a sulfate. The second product, KNO_3, is also soluble because it contains nitrate (rule 2). Therefore, no precipitation reaction occurs.

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Summary

In contrast to K_{sp}, the ion product (Q_{sp}) describes concentrations that are not necessarily equilibrium concentrations. Comparing Q and K_{sp} enables us to determine whether a precipitate will form when solutions of two soluble salts are mixed. Adding a common cation or common anion to a solution of a sparingly soluble salt shifts the solubility equilibrium in the direction predicted by Le Chatelier's principle. The solubility of the salt is almost always decreased by the presence of a common ion.

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7.4: The Effects of pH on Solubility

Learning Objectives

- To understand why the solubility of many compounds depends on pH.

The solubility of many compounds depends strongly on the pH of the solution. For example, the anion in many sparingly soluble salts is the conjugate base of a weak acid that may become protonated in solution. In addition, the solubility of simple binary compounds such as oxides and sulfides, both strong bases, is often dependent on pH. In this section, we discuss the relationship between the solubility of these classes of compounds and pH.

The Effect of Acid–Base Equilibria the Solubility of Salts

We begin our discussion by examining the effect of pH on the solubility of a representative salt, $\mathrm{M^+A^-}$, where $\mathrm{A^-}$ is the conjugate base of the weak acid HA. When the salt dissolves in water, the following reaction occurs:



with



The anion can also react with water in a hydrolysis reaction:



Because of the reaction described in Equation 7.4.1341, the predicted solubility of a sparingly soluble salt that has a basic anion such as S^{2-}, PO_4^{3-}, or CO_3^{2-} is increased. If instead a strong acid is added to the solution, the added H^+ will react essentially completely with A^- to form HA. This reaction decreases $[A^-]$, which decreases the magnitude of the ion product

$$Q = [\mathrm{M^+}][\mathrm{A^-}] \tag{7.4.1670}$$

According to Le Chatelier's principle, more MA will dissolve until $Q = K_{sp}$. Hence an acidic pH dramatically increases the solubility of virtually all sparingly soluble salts whose anion is the conjugate base of a weak acid. In contrast, pH has little to no effect on the solubility of salts whose anion is the conjugate base of a stronger weak acid or a strong acid, respectively (e.g., chlorides, bromides, iodides, and sulfates). For example, the hydroxide salt $Mg(OH)_2$ is relatively insoluble in water:



with



When acid is added to a saturated solution that contains excess solid $Mg(OH)_2$, the following reaction occurs, removing OH^- from solution:



The overall equation for the reaction of $Mg(OH)_2$ with acid is thus



As more acid is added to a suspension of $Mg(OH)_2$, the equilibrium shown in Equation 7.4.1346 is driven to the right, so more $Mg(OH)_2$ dissolves.

Such pH-dependent solubility is not restricted to salts that contain anions derived from water. For example, CaF_2 is a sparingly soluble salt:



with



When strong acid is added to a saturated solution of CaF_2, the following reaction occurs:



Because the forward reaction decreases the fluoride ion concentration, more CaF_2 dissolves to relieve the stress on the system. The net reaction of CaF_2 with strong acid is thus



Example 7.4.1 shows how to calculate the solubility effect of adding a strong acid to a solution of a sparingly soluble salt.

Sparingly soluble salts derived from weak acids tend to be more soluble in an acidic solution.

Example 7.4.1

Lead oxalate (PbC_2O_4), lead iodide (PbI_2), and lead sulfate ($PbSO_4$) are all rather insoluble, with K_{sp} values of 4.8×10^{-10}, 9.8×10^{-9}, and 2.53×10^{-8}, respectively. What effect does adding a strong acid, such as perchloric acid, have on their relative solubilities?

Given: K_{sp} values for three compounds

Asked for: relative solubilities in acid solution

Strategy:

Write the balanced chemical equation for the dissolution of each salt. Because the strongest conjugate base will be most affected by the addition of strong acid, determine the relative solubilities from the relative basicity of the anions.

Solution

The solubility Equilibria for the three salts are as follows:

$$PbC_2O_{4(s)} \rightleftharpoons Pb^{2+}(aq) + C_2O^{2-}_{4(aq)}$$

$$PbI_{2(s)} \rightleftharpoons Pb^{2+}(aq) + 2I^{-}(aq)$$

$$PbSO_{4(s)} \rightleftharpoons Pb^{2+}(aq) + SO^{2-}_{4(aq)}$$

The addition of a strong acid will have the greatest effect on the solubility of a salt that contains the conjugate base of a weak acid as the anion. Because HI is a strong acid, we predict that adding a strong acid to a saturated solution of PbI_2 will not greatly affect its solubility; the acid will simply dissociate to form H^+(aq) and the corresponding anion. In contrast, oxalate is the fully deprotonated form of oxalic acid (HO_2CCO_2H), which is

a weak diprotic acid (pK_{a1} = 1.23 and pK_{a2} = 4.19). Consequently, the oxalate ion has a significant affinity for one proton and a lower affinity for a second proton. Adding a strong acid to a saturated solution of lead oxalate will result in the following reactions:

$$C_2O^{2-}_{4(aq)} + H^+(aq) \rightarrow HO_2CCO^-_{2(aq)}$$

$$HO_2CCO^-_{2(aq)} + H^+(aq) \rightarrow HO_2CCO_2H(aq)$$

These reactions will decrease [$C_2O_4^{2-}$], causing more lead oxalate to dissolve to relieve the stress on the system.

The pK_a of HSO_4^- (1.99) is similar in magnitude to the pK_{a1} of oxalic acid, so adding a strong acid to a saturated solution of $PbSO_4$ will result in the following reaction:

$$SO^{2-}_{4(aq)} + H^+(aq) \rightleftharpoons HSO^-_{4(aq)}$$

Because HSO_4^- has a pKa of 1.99, this reaction will lie largely to the left as written. Consequently, we predict that the effect of added strong acid on the solubility of $PbSO_4$ will be significantly less than for PbC_2O_4.

Exercise 7.4.1

Which of the following insoluble salts—AgCl, Ag_2CO_3, Ag_3PO_4, and/or AgBr—will be substantially more soluble in 1.0 M HNO_3 than in pure water?

Answer

Ag_2CO_3 and Ag_3PO_4

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https://www.youtube.com/embed/XJ0s5SATZgQ?vq=hd1080

Solubility Products and pH: https://youtu.be/XJ0s5SATZgQ

Caves and their associated pinnacles and spires of stone provide one of the most impressive examples of pH-dependent solubility Equilbria(part (a) in Figure 7.4.1:). Perhaps the most familiar caves are formed from limestone, such as Carlsbad Caverns in New Mexico, Mammoth Cave in Kentucky, and Luray Caverns in Virginia. The primary reactions that are responsible for the formation of limestone caves are as follows:



Limestone deposits that form caves consist primarily of $CaCO_3$ from the remains of living creatures such as clams and corals, which used it for making structures such as shells. When a saturated solution of $CaCO_3$ in CO_2-rich water rises toward Earth's surface or is otherwise heated, CO_2 gas is released as the water warms. $CaCO_3$ then precipitates from the solution according to the following equation (part (b) in Figure 7.4.1:):



The forward direction is the same reaction that produces the solid called scale in teapots, coffee makers, water heaters, boilers, and other places where hard water is repeatedly heated.



Figure 7.4.1: The Chemistry of Cave Formation. (a) This cave in Campanet, Mallorca, Spain, and its associated formations are examples of pH-dependent solubility equilibriums. (b) A cave forms when groundwater containing atmospheric CO_2, forming an acidic solution, dissolves limestone ($CaCO_3$) in a process that may take tens of thousands of years. As groundwater seeps into a cave, water evaporates from the solution of $CaCO_3$ in CO_2-rich water, producing a supersaturated solution and a shift in equilibrium that causes precipitation of the $CaCO_3$. The deposited limestone eventually forms stalactites and stalagmites.

When groundwater-containing atmospheric CO_2 (Equations 7.4.1351 and 7.4.1352) finds its way into microscopic cracks in the limestone deposits, $CaCO_3$ dissolves in the acidic solution in the reverse direction of Equation 7.4.1354. The cracks gradually enlarge from 10–50 μm to 5–10 mm, a process that can take as long as 10,000 yr. Eventually, after about another 10,000 yr, a cave forms. Groundwater from the surface seeps into the cave and clings to the ceiling, where the water evaporates and causes the equilibrium in Equation 7.4.1354 to shift to the right. A circular layer of solid $CaCO_3$ is deposited, which eventually produces a long, hollow spire of limestone called a stalactite that grows down from the ceiling. Below, where the droplets land when they fall from the ceiling, a similar process causes another spire, called a stalagmite, to grow up. The same processes that carve out hollows below ground are also at work above ground, in some cases producing fantastically convoluted landscapes like that of Yunnan Province in China (Figure 7.4.2).

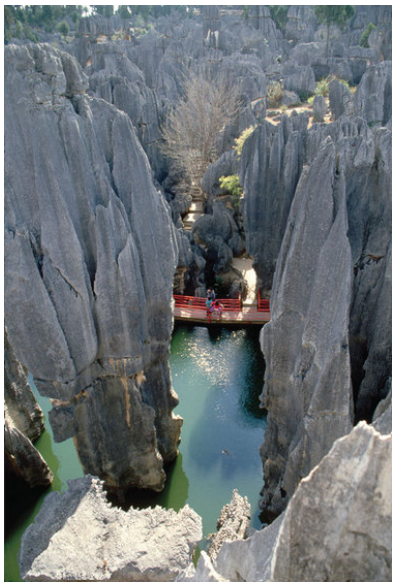


Figure 7.4.2: Solubility Equilbriain the Formation of Karst Landscapes. Landscapes such as the steep limestone pinnacles of the Stone Forest in Yunnan Province, China, are formed from the same process that produces caves and their associated formations.

Acidic, Basic, and Amphoteric Oxides and Hydroxides

One of the earliest classifications of substances was based on their solubility in acidic versus basic solution, which led to the classification of oxides and hydroxides as being either basic or acidic. **Basic oxides** and hydroxides either react with water to produce a basic solution or dissolve readily in aqueous acid. **Acidic oxides** or hydroxides either react with water to produce an acidic solution or are soluble in aqueous base. There is a clear correlation between the acidic or the basic character of an oxide and the position of the element combined with oxygen in the periodic table. Oxides of metallic elements are generally basic oxides, and oxides of nonmetallic elements are acidic oxides. Compare, for example, the reactions of a typical metal oxide, cesium oxide, and a typical nonmetal oxide, sulfur trioxide, with water:

[redacted]

Cesium oxide reacts with water to produce a basic solution of cesium hydroxide, whereas sulfur trioxide reacts with water to produce a solution of sulfuric acid—very different behaviors indeed

> Metal oxides generally react with water to produce basic solutions, whereas nonmetal oxides produce acidic solutions.

The difference in reactivity is due to the difference in bonding in the two kinds of oxides. Because of the low electronegativity of the metals at the far left in the periodic table, their oxides are best viewed as containing discrete M^{n+} cations and O^{2-} anions. At the other end of the spectrum are nonmetal oxides; due to their higher electronegativities, nonmetals form oxides with covalent bonds to oxygen. Because of the high electronegativity of oxygen, however, the covalent bond between oxygen and the other atom, E, is usually polarized: $E^{\delta+}$–$O^{\delta-}$. The atom E in these oxides acts as a Lewis acid that reacts with the oxygen atom of water to produce an oxoacid. Oxides of metals in high oxidation states also tend to be acidic oxides for the same reason: they contain covalent bonds to oxygen. An example of an acidic metal oxide is MoO_3, which is insoluble in both water and acid but dissolves in strong base to give solutions of the molybdate ion (MoO_4^{2-}):

[redacted]

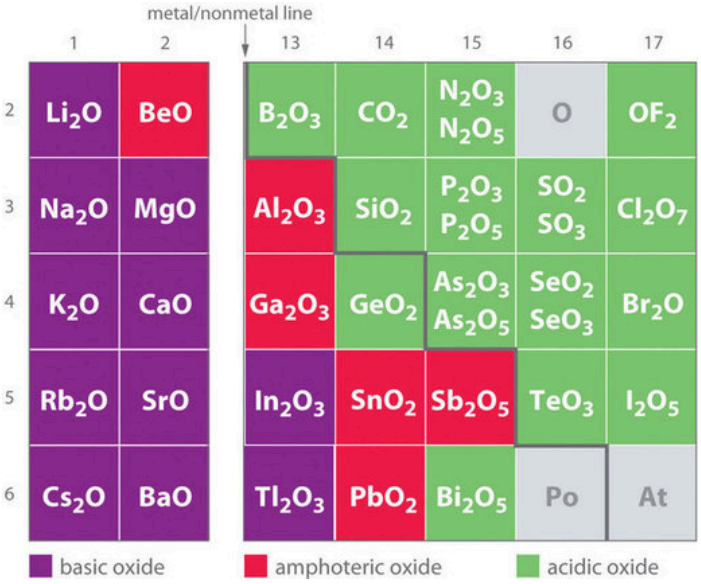


Figure 7.4.3: Classification of the Oxides of the Main Group Elements According to Their Acidic or Basic Character. There is a gradual transition from basic oxides to acidic oxides from the lower left to the upper right in the periodic table. Oxides of metallic elements are generally basic oxides, which either react with water to form a basic solution or dissolve in aqueous acid. In contrast, oxides of nonmetallic elements are acidic oxides, which either react with water to form an acidic solution or are soluble in aqueous base. Oxides of intermediate character, called amphoteric oxides, are located along a diagonal line between the two extremes. Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex ion. (Radioactive elements are not classified.)

As shown in Figure 7.4.3, there is a gradual transition from basic metal oxides to acidic nonmetal oxides as we go from the lower left to the upper right in the periodic table, with a broad diagonal band of oxides of intermediate character separating the

two extremes. Many of the oxides of the elements in this diagonal region of the periodic table are soluble in both acidic and basic solutions; consequently, they are called **amphoteric oxides** (from the Greek ampho, meaning "both," as in amphiprotic). Amphoteric oxides either dissolve in acid to produce water or dissolve in base to produce a soluble complex. As shown in Video 7.4.1, for example, mixing the amphoteric oxide $Cr(OH)_3$ (also written as $Cr_2O_3{\bullet}3H_2O$) with water gives a muddy, purple-brown suspension. Adding acid causes the $Cr(OH)_3$ to dissolve to give a bright violet solution of $Cr^{3+}(aq)$, which contains the $[Cr(H_2O)_6]^{3+}$ ion, whereas adding strong base gives a green solution of the $[Cr(OH)_4]^-$ ion. The chemical equations for the reactions are as follows:

[redacted]

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

https://www.youtube.com/embed/IQNcLH6OZK0?vq=hd1080

***Video** 7.4.1**:** Chromium(III) Hydroxide [$Cr(OH)_3$ or $Cr_2O_3{\bullet}3H_2O$] is an Example of an Amphoteric Oxide. All three beakers originally contained a suspension of brownish purple $Cr(OH)_3$(s) (center). When concentrated acid (6 M H_2SO_4) was added to the beaker on the left, $Cr(OH)_3$ dissolved to produce violet $[Cr(H_2O)_6]^{3+}$ ions and water. The addition of concentrated base (6 M NaOH) to the beaker on the right caused $Cr(OH)_3$ to dissolve, producing green $[Cr(OH)_4]^-$ ions. For a more complete description, see https://www.youtube.com/watch?v=IQNcLH6OZK0*

Example 7.4.2

Aluminum hydroxide, written as either $Al(OH)_3$ or $Al_2O_3{\bullet}3H_2O$, is amphoteric. Write chemical equations to describe the dissolution of aluminum hydroxide in (a) acid and (b) base.

Given: amphoteric compound

Asked for: dissolution reactions in acid and base

Strategy:

Using Equations 7.4.1358 and 7.4.1359 as a guide, write the dissolution reactions in acid and base solutions.

Solution

a. An acid donates protons to hydroxide to give water and the hydrated metal ion, so aluminum hydroxide, which contains three OH^- ions per Al, needs three H^+ ions:

$$Al(OH)_{3(s)} + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$$

In aqueous solution, Al^{3+} forms the complex ion $[Al(H_2O)_6]^{3+}$.

b. In basic solution, OH^- is added to the compound to produce a soluble and stable poly(hydroxo) complex:

$$Al(OH)_{3(s)} + OH^-(aq) \rightarrow [Al(OH)_4]^-(aq)$$

Exercise 7.4.2

Copper(II) hydroxide, written as either $Cu(OH)_2$ or $CuO{\bullet}H_2O$, is *amphoteric*. Write chemical equations that describe the dissolution of cupric hydroxide both in an acid and in a base.

Answer

$$Cu(OH)_{2(s)} + 2H^+(aq) \rightarrow Cu^{2+}(aq) + 2H_2O(l)$$

$$Cu(OH)_{2(s)} + 2OH^-(aq) \rightarrow [Cu(OH)_4]^2_{-(aq)}$$

Selective Precipitation Using pH

Many dissolved metal ions can be separated by the selective precipitation of the cations from solution under specific conditions. In this technique, pH is often used to control the concentration of the anion in solution, which controls which cations precipitate.

> The concentration of anions in solution can often be controlled by adjusting the pH, thereby allowing the selective precipitation of cations.

Suppose, for example, we have a solution that contains 1.0 mM Zn^{2+} and 1.0 mM Cd^{2+} and want to separate the two metals by selective precipitation as the insoluble sulfide salts, ZnS and CdS. The relevant solubility equilbria can be written as follows:

[redacted]

with

[redacted]

and

[redacted]

with

[redacted]

Because the S^{2-} ion is quite basic and reacts extensively with water to give HS^- and OH^-, the solubility equilbria are more accurately written as $MS(s) \rightleftharpoons M^{2+}(aq) + HS^-(aq) + OH^-$ rather than $MS(s) \rightleftharpoons M^{2+}(aq) + S^{2-}(aq)$. Here we use the simpler form involving S^{2-}, which is justified because we take the reaction of S^{2-} with water into account later in the solution, arriving at

the same answer using either equilibrium equation.

The sulfide concentrations needed to cause ZnS and CdS to precipitate are as follows:

[redacted]

and

[redacted]

Thus sulfide concentrations between 1.6 × 10^{-21} M and 8.0 × 10^{-24} M will precipitate CdS from solution but not ZnS. How do we obtain such low concentrations of sulfide? A saturated aqueous solution of H_2S contains 0.10 M H_2S at 20°C. The p$K_{a1}$for H_2S is 6.97, and pK_{a2} corresponding to the formation of [S^{2-}] is 12.90. The equations for these reactions are as follows:

[redacted]

with

[redacted]

with

[redacted]

We can show that the concentration of S^{2-} is 1.3 × 10^{-13} by comparing K_{a1} and K_{a2} and recognizing that the contribution to [H^+] from the dissociation of HS^- is negligible compared with [H^+] from the dissociation of H_2S. Thus substituting 0.10 M in the equation for K_{a1} for the concentration of H_2S, which is essentially constant regardless of the pH, gives the following:

[redacted]

Substituting this value for [H^+] and [HS^-] into the equation for K_{a2},

$$K_{a2} = 1.3 \times 10^{-13} = \frac{[H^+][S^{2-}]}{[HS^-]} = \frac{(1.1 \times 10^{-4}\ M)x}{1.1 \times 10^{-4}\ M} = x = [S^{2-}] \tag{7.4.1671}$$

Although [S^{2-}] in an H_2S solution is very low (1.3 × 10^{-13} M), bubbling H_2S through the solution until it is saturated would precipitate both metal ions because the concentration of S^{2-} would then be much greater than 1.6 × 10^{-21} M. Thus we must adjust [S^{2-}] to stay within the desired range. The most direct way to do this is to adjust [H^+] by adding acid to the H_2S solution (recall Le Chatelier's principle), thereby driving the equilibrium in Equation 7.4.1373 to the left. The overall equation for the dissociation of H_2S is as follows:

[redacted]

Now we can use the equilibrium constant K for the overall reaction, which is the product of K_{a1} and K_{a2}, and the concentration of H_2S in a saturated solution to calculate the H^+ concentration needed to produce [S^{2-}] of 1.6 × 10^{-21} M:

[redacted]

Thus adding a strong acid such as HCl to make the solution 0.94 M in H^+ will prevent the more soluble ZnS from precipitating while ensuring that the less soluble CdS will precipitate when the solution is saturated with H_2S.

Example 7.4.3

A solution contains 0.010 M Ca^{2+} and 0.010 M La^{3+}. What concentration of HCl is needed to precipitate $La_2(C_2O_4)_3•9H_2O$ but not $Ca(C_2O_4)•H_2O$ if the concentration of oxalic acid is 1.0 M? K_{sp} values are 2.32×10^{-9} for $Ca(C_2O_4)$ and 2.5×10^{-27} for $La_2(C_2O_4)_3$; $pK_{a1} = 1.25$ and $pK_{a2} = 3.81$ for oxalic acid.

Given: concentrations of cations, K_{sp} values, and concentration and pK_a values for oxalic acid

Asked for: concentration of HCl needed for selective precipitation of $La_2(C_2O_4)_3$

Strategy:

A. Write each solubility product expression and calculate the oxalate concentration needed for precipitation to occur. Determine the concentration range needed for selective precipitation of $La_2(C_2O_4)_3•9H_2O$.
B. Add the equations for the first and second dissociations of oxalic acid to get an overall equation for the dissociation of oxalic acid to oxalate. Substitute the $[ox^{2-}]$ needed to precipitate $La_2(C_2O_4)_3•9H_2O$ into the overall equation for the dissociation of oxalic acid to calculate the required $[H^+]$.

Solution

A Because the salts have different stoichiometries, we cannot directly compare the magnitudes of the solubility products. Instead, we must use the equilibrium constant expression for each solubility product to calculate the concentration of oxalate needed for precipitation to occur. Using ox^{2-} for oxalate, we write the solubility product expression for calcium oxalate as follows:

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (0.010)[ox^{2-}] = 2.32 \times 10^{-9}$$

$$[ox^{2-}] = 2.32 \times 10^{-7}\ M$$

The expression for lanthanum oxalate is as follows:

$$K_{sp} = [La^{3+}]^2[ox^{2-}]^3 = (0.010)^2[ox^{2-}]^3 = 2.5 \times 10^{-27}$$

$$[ox^{2-}] = 2.9 \times 10^{-8}\ M$$

Thus lanthanum oxalate is less soluble and will selectively precipitate when the oxalate concentration is between $2.9 \times 10^{-8} M$ and $2.32 \times 10^{-7} M$.

B To prevent Ca^{2+} from precipitating as calcium oxalate, we must add enough H^+ to give a maximum oxalate concentration of 2.32×10^{-7} M. We can calculate the required $[H^+]$ by using the overall equation for the dissociation of oxalic acid to oxalate:

$$HO_2CCO_2H(aq) \rightleftharpoons 2H^+(aq) + C_2O_{4(aq)}^{2-} \tag{7.4.1674}$$

$$K = K_{a1}K_{a2} = (10^{-1.25})(10^{-3.81}) = 10^{-5.06} = 8.7 \times 10^{-6}$$

Substituting the desired oxalate concentration into the equilibrium constant expression,

$$8.7 \times 10^{-6} = \frac{[H^+]^2[ox^{2-}]}{[HO_2CCO_2H]} = \frac{[H^+]^2(2.32 \times 10^{-7})}{1.0} \quad (7.4.1675)$$

$$[H^+] = 6.1\ M \quad (7.4.1676)$$

Thus adding enough HCl to give $[H^+]$ = 6.1 M will cause only $La_2(C_2O_4)_3 \bullet 9H_2O$ to precipitate from the solution.

Exercise 7.4.3

A solution contains 0.015 M Fe^{2+} and 0.015 M Pb^{2+}. What concentration of acid is needed to ensure that Pb^{2+} precipitates as PbS in a saturated solution of H_2S, but Fe^{2+} does not precipitate as FeS? K_{sp} values are 6.3×10^{-18} for FeS and 8.0×10^{-28} for PbS.

Answer

0.018 M H^+

Summary

The anion in sparingly soluble salts is often the conjugate base of a weak acid that may become protonated in solution, so the solubility of simple oxides and sulfides, both strong bases, often depends on pH. The anion in many sparingly soluble salts is the conjugate base of a weak acid. At low pH, protonation of the anion can dramatically increase the solubility of the salt. Oxides can be classified as acidic oxides or basic oxides. Acidic oxides either react with water to give an acidic solution or dissolve in strong base; most acidic oxides are nonmetal oxides or oxides of metals in high oxidation states. Basic oxides either react with water to give a basic solution or dissolve in strong acid; most basic oxides are oxides of metallic elements. Oxides or hydroxides that are soluble in both acidic and basic solutions are called amphoteric oxides. Most elements whose oxides exhibit amphoteric behavior are located along the diagonal line separating metals and nonmetals in the periodic table. In solutions that contain mixtures of dissolved metal ions, the pH can be used to control the anion concentration needed to selectively precipitate the desired cation.

Contributors and Attributions

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7.5: Complex Ions and Solubility

Learning Objectives

- To be introduced to complex ions, including ligands.

Previously, you learned that metal ions in aqueous solution are hydrated—that is, surrounded by a shell of usually four or six water molecules. A hydrated ion is one kind of a **complex ion** (or, simply, complex), a species formed between a central metal ion and one or more surrounding **ligands**, molecules or ions that contain at least one lone pair of electrons, such as the $[Al(H_2O)_6]^{3+}$ ion.

A complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base. Small, highly charged metal ions, such as Cu^{2+} or Ru^{3+}, have the greatest tendency to act as Lewis acids, and consequently, they have the greatest tendency to form complex ions.

As an example of the formation of complex ions, consider the addition of ammonia to an aqueous solution of the hydrated Cu^{2+} ion {$[Cu(H_2O)_6]^{2+}$}. Because it is a stronger base than H_2O, ammonia replaces the water molecules in the hydrated ion to form the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion. Formation of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex is accompanied by a dramatic color change, as shown in Figure 7.5.1. The solution changes from the light blue of $[Cu(H_2O)_6]^{2+}$ to the blue-violet characteristic of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion.



Figure 7.5.1: The Formation of Complex Ions. An aqueous solution of $CuSO_4$ consists of hydrated Cu^{2+} ions in the form of pale blue $[Cu(H_2O)_6]^{2+}$ (left). The addition of aqueous ammonia to the solution results in the formation of the intensely blue-violet $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions, usually written as $[Cu(NH_3)_4]^{2+}$ ion (right) because ammonia, a stronger base than H_2O, replaces water molecules from the hydrated Cu^{2+} ion. For a more complete description, see www.youtube.com/watch?v=IQNcLH6OZK0.

The Formation Constant

The replacement of water molecules from $[Cu(H_2O)_6]^{2+}$ by ammonia occurs in sequential steps. Omitting the water molecules

bound to Cu^{2+} for simplicity, we can write the equilibrium reactions as follows:



The sum of the stepwise reactions is the overall equation for the formation of the complex ion: The hydrated Cu^{2+} ion contains six H_2O ligands, but the complex ion that is produced contains only four NH_3 ligands, not six.



The equilibrium constant for the formation of the complex ion from the hydrated ion is called the **formation constant (K_f)**. The equilibrium constant expression for K_f has the same general form as any other equilibrium constant expression. In this case, the expression is as follows:



> The formation constant (K_f) has the same general form as any other equilibrium constant expression.

Water, a pure liquid, does not appear explicitly in the equilibrium constant expression, and the hydrated $Cu^{2+}(aq)$ ion is represented as Cu^{2+} for simplicity. As for any equilibrium, the larger the value of the equilibrium constant (in this case, K_f), the more stable the product. With $K_f = 2.1 \times 10^{13}$, the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is very stable. The formation constants for some common complex ions are listed in Table 7.5.1.

Table 7.5.1: Common Complex Ions

	Complex Ion	Equilibrium Equation	K_f
Ammonia Complexes	$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \diamond [Ag(NH_3)_2]^+$	1.1×10^7
	$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \diamond [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
	$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \diamond [Ni(NH_3)_6]^{2+}$	5.5×10^8
Cyanide Complexes	$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \diamond [Ag(CN)_2]^-$	1.1×10^{18}
	$[Ni(CN)_4]^{2-}$	$Ni^{2+} + 4CN^- \diamond [Ni(CN)_4]^{2-}$	2.2×10^{31}
	$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \diamond [Fe(CN)_6]^{3-}$	1×10^{42}
Hydroxide Complexes	$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4OH^- \diamond [Zn(OH)_4]^{2-}$	4.6×10^{17}
	$[Cr(OH)_4]^-$	$Cr^{3+} + 4OH^- \diamond [Cr(OH)_4]^-$	8.0×10^{29}
Halide Complexes	$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \diamond [HgCl_4]^{2-}$	1.2×10^{15}
	$[CdI_4]^{2-}$	$Cd^{2+} + 4I \diamond [CdI_4]^{2-}$	2.6×10^5
	$[AlF_6]^{3-}$	$Al^{3+} + 6F^- \diamond [AlF_6]^{3-}$	6.9×10^{19}
Other Complexes	$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \diamond [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \diamond [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}

***Reported values are overall formation constants. Source: Data from Lange's Handbook of Chemistry, 15th ed. (1999).**

Example 7.5.1

If 12.5 g of $Cu(NO_3)_2 \cdot 6\,H_2O$ is added to 500 mL of 1.00 M aqueous ammonia, what is the equilibrium concentration of $Cu^{2+}(aq)$?

Given: mass of Cu^{2+} salt and volume and concentration of ammonia solution

Asked for: equilibrium concentration of $Cu^{2+}(aq)$

Strategy:

A. Calculate the initial concentration of Cu^{2+} due to the addition of copper(II) nitrate hexahydrate. Use the stoichiometry of the reaction shown in Equation 7.5.1387 to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations of all species in solution.
B. Substitute the final concentrations into the expression for the formation constant (Equation 7.5.1388) to calculate the equilibrium concentration of $Cu^{2+}(aq)$.

Solution

Adding an ionic compound that contains Cu^{2+} to an aqueous ammonia solution will result in the formation of $[Cu(NH_3)_4]^{2+}(aq)$, as shown in Equation 7.5.1387. We assume that the volume change caused by adding solid copper(II) nitrate to aqueous ammonia is negligible.

A The initial concentration of Cu^{2+} from the amount of added copper nitrate prior to any reaction is as follows:

$$12.5 \cancel{\text{ g}}\ \text{Cu(NO}_3)_2 \cdot 6\text{H}_2\text{O} \left(\frac{1\ \text{mol}}{295.65 \cancel{\text{ g}}}\right) \left(\frac{1}{500\ \cancel{\text{mL}}}\right) \left(\frac{1000\ \cancel{\text{mL}}}{1\ \text{L}}\right) = 0.0846\ \text{M} \tag{7.5.1681}$$

Because the stoichiometry of the reaction is four NH_3 to one Cu^{2+}, the amount of NH_3 required to react completely with the Cu^{2+} is 4(0.0846) = 0.338 M. The concentration of ammonia after complete reaction is 1.00 M − 0.338 M = 0.66 M. These results are summarized in the first two lines of the following table. Because the equilibrium constant for the reaction is large (2.1×10^{13}), the equilibrium will lie far to the right. Thus we will assume that the formation of $[Cu(NH_3)_4]^{2+}$ in the first step is complete and allow some of it to dissociate into Cu^{2+} and NH_3 until equilibrium has been reached. If we define *x* as the amount of Cu^{2+} produced by the dissociation reaction, then the stoichiometry of the reaction tells us that the change in the concentration of $[Cu(NH_3)_4]^{2+}$ is *–x*, and the change in the concentration of ammonia is *+4x*, as indicated in the table. The final concentrations of all species (in the bottom row of the table) are the sums of the concentrations after complete reaction and the changes in concentrations.

$$Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

	$[Cu^{2+}]$	$[NH_3]$	$[[Cu(NH_3)_4]^{2+}]$
initial	0.0846	1.00	0
after complete reaction	0	0.66	0.0846
change	*+x*	*+4x*	*–x*
final	*x*	0.66 + 4*x*	0.0846 – *x*

B Substituting the final concentrations into the expression for the formation constant (Equation 7.5.1388) and assuming that *x* << 0.0846, which allows us to remove *x* from the sum and difference,

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{0.0846 - x}{x(0.66 + 4x)^4} \approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13}$$

$$x = 2.1 \times 10^{-14}$$

The value of *x* indicates that our assumption was justified. The equilibrium concentration of Cu^{2+}(aq) in a 1.00 M ammonia solution is therefore 2.1×10^{-14} M.

Exercise 7.5.1

The ferrocyanide ion $\{[Fe(CN)_6]^{4-}\}$ is very stable, with a K_f of 1×10^{35}. Calculate the concentration of cyanide ion in equilibrium with a 0.65 M solution of $K_4[Fe(CN)_6]$.

Answer

2×10^{-6} M

The Effect of the Formation of Complex Ions on Solubility

What happens to the solubility of a sparingly soluble salt if a ligand that forms a stable complex ion is added to the solution? One such example occurs in conventional black-and-white photography. Recall that black-and-white photographic film contains light-sensitive microcrystals of AgBr, or mixtures of AgBr and other silver halides. AgBr is a sparingly soluble salt, with a K_{sp} of 5.35×10^{-13} at 25°C. When the shutter of the camera opens, the light from the object being photographed strikes some of the crystals on the film and initiates a photochemical reaction that converts AgBr to black Ag metal. Well-formed, stable negative images appear in tones of gray, corresponding to the number of grains of AgBr converted, with the areas exposed to the most light being darkest. To fix the image and prevent more AgBr crystals from being converted to Ag metal during processing of the film, the unreacted AgBr on the film is removed using a complexation reaction to dissolve the sparingly soluble salt.

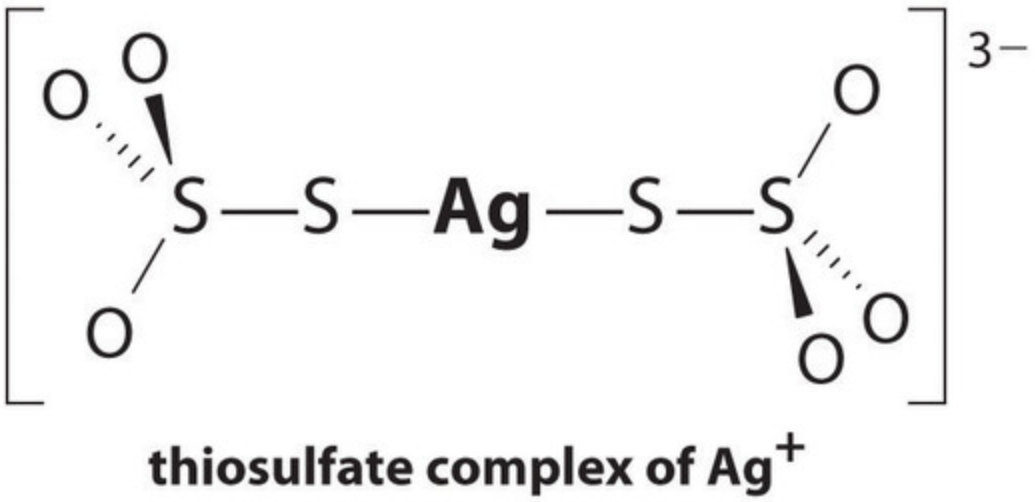
The reaction for the dissolution of silver bromide is as follows:

[redacted]

with

[redacted]

The equilibrium lies far to the left, and the equilibrium concentrations of Ag^+ and Br^- ions are very low (7.31×10^{-7} M). As a result, removing unreacted AgBr from even a single roll of film using pure water would require tens of thousands of liters of water and a great deal of time. Le Chatelier's principle tells us, however, that we can drive the reaction to the right by removing one of the products, which will cause more AgBr to dissolve. Bromide ion is difficult to remove chemically, but silver ion forms a variety of stable two-coordinate complexes with neutral ligands, such as ammonia, or with anionic ligands, such as cyanide or thiosulfate ($S_2O_3^{2-}$). In photographic processing, excess AgBr is dissolved using a concentrated solution of sodium thiosulfate.



thiosulfate complex of Ag^+

The reaction of Ag^+ with thiosulfate is as follows:

[redacted]

with

[redacted]

The magnitude of the equilibrium constant indicates that almost all Ag^+ ions in solution will be immediately complexed by thiosulfate to form $[Ag(S_2O_3)_2]^{3-}$. We can see the effect of thiosulfate on the solubility of AgBr by writing the appropriate reactions and adding them together:

[redacted]

Comparing K with K_{sp} shows that the formation of the complex ion increases the solubility of AgBr by approximately 3×10^{13}. The dramatic increase in solubility combined with the low cost and the low toxicity explains why sodium thiosulfate is almost universally used for developing black-and-white film. If desired, the silver can be recovered from the thiosulfate solution using any of several methods and recycled.

> If a complex ion has a large K_f, the formation of a complex ion can dramatically increase the solubility of sparingly soluble salts.

Example 7.5.2

Due to the common ion effect, we might expect a salt such as AgCl to be much less soluble in a concentrated solution of KCl than in water. Such an assumption would be incorrect, however, because it ignores the fact that silver ion tends to form a two-coordinate complex with chloride ions ($AgCl_2^-$). Calculate the solubility of AgCl in each situation:

a. in pure water
b. in 1.0 M KCl solution, ignoring the formation of any complex ions
c. the same solution as in part (b) except taking the formation of complex ions into account, assuming that $AgCl_2^-$ is the only Ag^+ complex that forms in significant concentrations

At 25°C, $K_{sp} = 1.77 \times 10^{-10}$ for AgCl and $K_f = 1.1 \times 10^5$ for $AgCl_2^-$.

Given: K_{sp} of AgCl, K_f of $AgCl_2^-$, and KCl concentration

Asked for: solubility of AgCl in water and in KCl solution with and without the formation of complex ions

Strategy:

A. Write the solubility product expression for AgCl and calculate the concentration of Ag^+ and Cl^- in water.
B. Calculate the concentration of Ag^+ in the KCl solution.
C. Write balanced chemical equations for the dissolution of AgCl and for the formation of the $AgCl_2^-$ complex. Add the two equations and calculate the equilibrium constant for the overall equilibrium.
D. Write the equilibrium constant expression for the overall reaction. Solve for the concentration of the complex ion.

Solution

a. **A** If we let x equal the solubility of AgCl, then at equilibrium [Ag+] = $[Cl^-] = x$ M. Substituting this value into the solubility product expression,

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = x^2 = 1.77\times10^{-10}$$

$$x = 1.33\times10^{-5}$$

Thus the solubility of AgCl in pure water at 25°C is 1.33×10^{-5} M.

b. **B** If x equals the solubility of AgCl in the KCl solution, then at equilibrium $[Ag^+] = x$ M and $[Cl^-] = (1.0 + x)$ M. Substituting these values into the solubility product expression and assuming that $x << 1.0$,

$$K_{sp} = [Ag^+][Cl^-] = (x)(1.0 + x) \approx x(1.0) = 1.77\times10^{-10} = x$$

If the common ion effect were the only important factor, we would predict that AgCl is approximately five orders of magnitude less soluble in a 1.0 M KCl solution than in water.

c. **C** To account for the effects of the formation of complex ions, we must first write the equilibrium equations for both the dissolution and the formation of complex ions. Adding the equations corresponding to K_{sp} and K_f gives us an equation that describes the dissolution of AgCl in a KCl solution. The equilibrium constant for the reaction is therefore the product of K_{sp} and K_f:

$$\mathrm{AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)} \quad K_{sp} = 1.77 \times 10^{-10} \tag{7.5.1685}$$

$$\mathrm{Ag^+(aq) + 2Cl^- \rightleftharpoons [AgCl_2]^-} \quad K_f = 1.1 \times 10^5 \tag{7.5.1686}$$

$$\mathrm{AgCl(s) + Cl^- \rightleftharpoons [AgCl_2]^-} \quad K = K_{sp}K_f = 1.9 \times 10^{-5} \tag{7.5.1687}$$

D If we let x equal the solubility of AgCl in the KCl solution, then at equilibrium $[AgCl_2^-] = x$ and $[Cl^-] = 1.0 - x$. Substituting these quantities into the equilibrium constant expression for the net reaction and assuming that $x << 1.0$,

$$K = \frac{[\mathrm{AgCl_2^-}]}{[\mathrm{Cl^-}]} = \frac{x}{1.0 - x} \approx 1.9 \times 10^{-5} = x$$

That is, AgCl dissolves in 1.0 M KCl to produce a 1.9×10^{-5} M solution of the $AgCl_2^-$ complex ion. Thus we predict that AgCl has approximately the same solubility in a 1.0 M KCl solution as it does in pure water, which is 10^5 times greater than that predicted based on the common ion effect. (In fact, the measured solubility of AgCl in 1.0 M KCl is almost a factor of 10 greater than that in pure water, largely due to the formation of other chloride-containing complexes.)

Exercise 7.5.2

Calculate the solubility of mercury(II) iodide (HgI_2) in each situation:

a. pure water
b. a 3.0 M solution of NaI, assuming $[HgI_4]^{2-}$ is the only Hg-containing species present in significant amounts

$$K_{sp} = 2.9 \times 10^{-29} \text{ for } HgI_2 \text{ and } K_f = 6.8 \times 10^{29} \text{ for } [HgI_4]^{2-}.$$

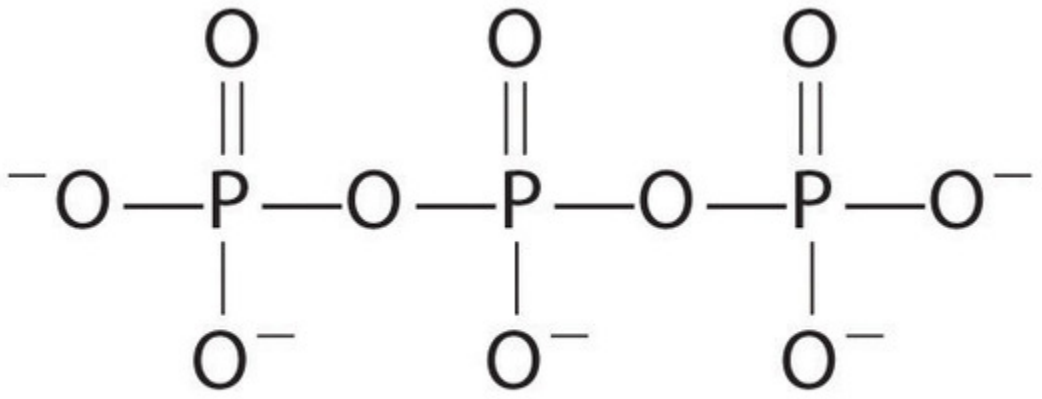
Answer a

1.9×10^{-10} M

Answer a

1.4 M

Complexing agents, molecules or ions that increase the solubility of metal salts by forming soluble metal complexes, are common components of laundry detergents. Long-chain carboxylic acids, the major components of soaps, form insoluble salts with Ca^{2+} and Mg^{2+}, which are present in high concentrations in "hard" water. The precipitation of these salts produces a bathtub ring and gives a gray tinge to clothing. Adding a complexing agent such as pyrophosphate ($O_3POPO_3^{4-}$, or $P_2O_7^{4-}$) or triphosphate ($P_3O_{10}^{5-}$) to detergents prevents the magnesium and calcium salts from precipitating because the equilibrium constant for complex-ion formation is large:



triphosphate

[redacted]

with

[redacted]

However, phosphates can cause environmental damage by promoting eutrophication, the growth of excessive amounts of algae in a body of water, which can eventually lead to large decreases in levels of dissolved oxygen that kill fish and other aquatic organisms. Consequently, many states in the United States have banned the use of phosphate-containing detergents, and France has banned their use beginning in 2007. "Phosphate-free" detergents contain different kinds of complexing agents, such as derivatives of acetic acid or other carboxylic acids. The development of phosphate substitutes is an area of intense research.

Commercial water softeners also use a complexing agent to treat hard water by passing the water over ion-exchange resins, which are complex sodium salts. When water flows over the resin, sodium ion is dissolved, and insoluble salts precipitate onto the resin surface. Water treated in this way has a saltier taste due to the presence of Na^+, but it contains fewer dissolved minerals.

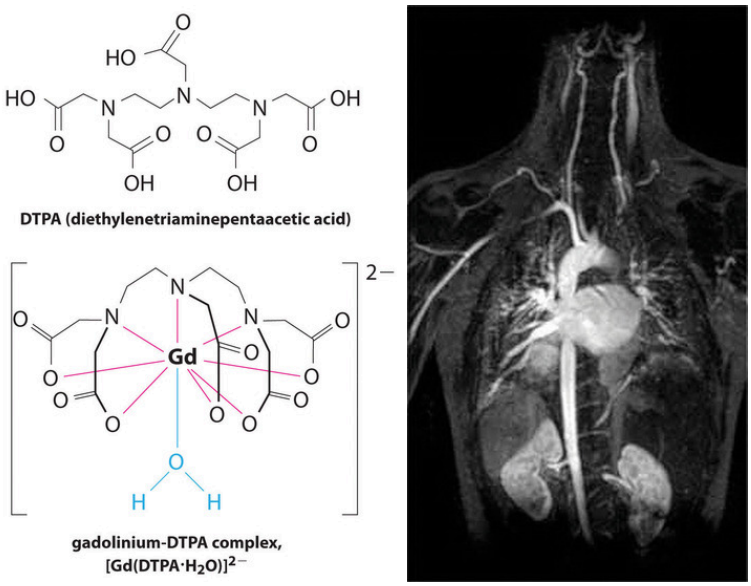


Figure 7.5.2: An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

Another application of complexing agents is found in medicine. Unlike x-rays, magnetic resonance imaging (MRI) can give relatively good images of soft tissues such as internal organs. MRI is based on the magnetic properties of the ^1H nucleus of hydrogen atoms in water, which is a major component of soft tissues. Because the properties of water do not depend very much on whether it is inside a cell or in the blood, it is hard to get detailed images of these tissues that have good contrast. To solve this problem, scientists have developed a class of metal complexes known as “MRI contrast agents.” Injecting an MRI contrast agent into a patient selectively affects the magnetic properties of water in cells of normal tissues, in tumors, or in blood vessels and allows doctors to “see” each of these separately (Figure 7.5.2). One of the most important metal ions for this application is Gd^{3+}, which with seven unpaired electrons is highly paramagnetic. Because $Gd^{3+}(aq)$ is quite toxic, it must be administered as a very stable complex that does not dissociate in the body and can be excreted intact by the kidneys. The complexing agents used for gadolinium are ligands such as $DTPA^{5-}$ (diethylene triamine pentaacetic acid), whose fully protonated form is shown here.

Summary

The formation of complex ions can substantially increase the solubility of sparingly soluble salts if the complex ion has a large K_f. A complex ion is a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons. Small, highly charged metal ions have the greatest tendency to act as Lewis acids and form complex ions. The equilibrium constant for the formation of the complex ion is the formation constant (K_f). The formation of a complex ion by adding a complexing agent increases the solubility of a compound.

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VII: SOLUBILITY AND PRECIPITATION EQUILIBRIA

Solubility equilibrium is a type of dynamic equilibrium. It exists when a chemical compound in the solid state is in chemical equilibrium with a solution of that compound. The solid may dissolve unchanged, with dissociation or with chemical reaction with another constituent of the solvent, such as acid or alkali. Each type of equilibrium is characterized by a temperature-dependent equilibrium constant. Solubility equilibria are important in pharmaceutical, environmental and many other scenarios.

7.1: The Nature of Solubility Equilibria

7.2: Ionic Equilibria between Solids and Solutions

7.3: Precipitation and the Solubility Product

7.4: The Effects of pH on Solubility

7.5: Complex Ions and Solubility

7.6: A Deeper Look - Selective Precipitation of Ions

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7.6: A Deeper Look - Selective Precipitation of Ions

Learning Objectives

- To know how to separate metal ions by selective precipitation.
- To understand how several common metal cations can be identified in a solution using selective precipitation.

The composition of relatively complex mixtures of metal ions can be determined using **qualitative analysis**, a procedure for discovering the identity of metal ions present in the mixture (rather than quantitative information about their amounts). The procedure used to separate and identify more than 20 common metal cations from a single solution consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively less selective until almost all of the metal ions are precipitated, as illustrated in Figure 7.6.1.

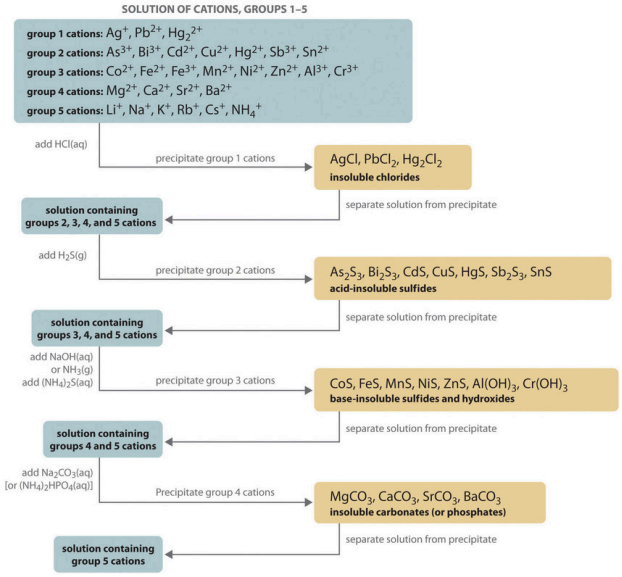


Figure 7.6.1: Steps in a Typical Qualitative Analysis Scheme for a Solution That Contains Several Metal Ions

Group 1: Insoluble Chlorides

Most metal chloride salts are soluble in water; only Ag^+, Pb^{2+}, and $Hg_2{}^{2+}$ form chlorides that precipitate from water. Thus the first step in a qualitative analysis is to add about 6 M HCl, thereby causing $AgCl$, $PbCl_2$, and/or Hg_2Cl_2 to precipitate. If no precipitate forms, then these cations are not present in significant amounts. The precipitate can be collected by filtration or centrifugation.

Group 2: Acid-Insoluble Sulfides

Next, the acidic solution is saturated with H_2S gas. Only those metal ions that form very insoluble sulfides, such as As^{3+}, Bi^{3+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Sb^{3+}, and Sn^{2+}, precipitate as their sulfide salts under these acidic conditions. All others, such as Fe^{2+} and Zn^{2+}, remain in solution. Once again, the precipitates are collected by filtration or centrifugation.

Group 3: Base-Insoluble Sulfides (and Hydroxides)

Ammonia or $NaOH$ is now added to the solution until it is basic, and then $(NH_4)_2S$ is added. This treatment removes any remaining cations that form insoluble hydroxides or sulfides. The divalent metal ions Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} precipitate as their

sulfides, and the trivalent metal ions Al^{3+} and Cr^{3+} precipitate as their hydroxides: $Al(OH)_3$ and $Cr(OH)_3$. If the mixture contains Fe^{3+}, sulfide reduces the cation to Fe^{2+}, which precipitates as FeS.

Group 4: Insoluble Carbonates or Phosphates

The next metal ions to be removed from solution are those that form insoluble carbonates and phosphates. When Na_2CO_3 is added to the basic solution that remains after the precipitated metal ions are removed, insoluble carbonates precipitate and are collected. Alternatively, adding $(NH_4)_2HPO_4$ causes the same metal ions to precipitate as insoluble phosphates.

Group 5: Alkali Metals

At this point, we have removed all the metal ions that form water-insoluble chlorides, sulfides, carbonates, or phosphates. The only common ions that might remain are any alkali metals (Li^+, Na^+, K^+, Rb^+, and Cs^+) and ammonium ($NH_4{}^+$). We now take a second sample from the original solution and add a small amount of $NaOH$ to neutralize the ammonium ion and produce NH_3. (We cannot use the same sample we used for the first four groups because we added ammonium to that sample in earlier steps.) Any ammonia produced can be detected by either its odor or a litmus paper test. A flame test on another original sample is used to detect sodium, which produces a characteristic bright yellow color. The other alkali metal ions also give characteristic colors in flame tests, which allows them to be identified if only one is present.

Metal ions that precipitate together are separated by various additional techniques, such as forming complex ions, changing the pH of the solution, or increasing the temperature to redissolve some of the solids. For example, the precipitated metal chlorides of group 1 cations, containing Ag^+, Pb^{2+}, and $Hg_2{}^{2+}$, are all quite insoluble in water. Because $PbCl_2$ is much more soluble in hot water than are the other two chloride salts, however, adding water to the precipitate and heating the resulting slurry will dissolve any $PbCl_2$ present. Isolating the solution and adding a small amount of Na_2CrO_4 solution to it will produce a bright yellow precipitate of $PbCrO_4$ if Pb^{2+} were in the original sample (Figure 7.6.2).



Figure 7.6.2: When a small amount of Na_2CrO_4 solution is added to a sample containing Pb^{2+} ions in water, a bright yellow precipitate of $PbCrO_4$ forms. (CC BY-SA 3.0 Unported; PRHaney via Wikipedia).

As another example, treating the precipitates from group 1 cations with aqueous ammonia will dissolve any $AgCl$ because Ag^+ forms a stable complex with ammonia: $[Ag(NH_3)_2]^+$. In addition, Hg_2Cl_2 disproportionates in ammonia.

$$2\,Hg_2{}^{2+} \rightarrow Hg + Hg^{2+}$$

to form a black solid that is a mixture of finely divided metallic mercury and an insoluble mercury(II) compound, which is separated from solution:

$$Hg_2Cl_2\,(s) + 2\,NH_3\,(aq) \rightarrow Hg\,(l) + Hg(NH_2)Cl\,(s) + NH_4^+\,(aq) + Cl^-\,(aq)$$

Any silver ion in the solution is then detected by adding HCl, which reverses the reaction and gives a precipitate of white AgCl that slowly darkens when exposed to light:

$$[\mathrm{Ag(NH_3)_2}]^+\,(\mathrm{aq}) + 2\,\mathrm{H}^+\,(\mathrm{aq}) + \mathrm{Cl}^-\,(\mathrm{aq}) \;\rightarrow \mathrm{AgCl}\,(\mathrm{s}) + 2\,\mathrm{NH}_4^+\,(\mathrm{aq})$$

Similar but slightly more complex reactions are also used to separate and identify the individual components of the other groups.

Summary

In qualitative analysis, the identity, not the amount, of metal ions present in a mixture is determined. The technique consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions. Consecutive precipitation steps become progressively less selective until almost all the metal ions are precipitated. Other additional steps are needed to separate metal ions that precipitate together.

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