CHEM 210: SOUTHWESTERN



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Chem 210 - Southwestern

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Licensing

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CHAPTER OVERVIEW

10: Solids, Liquids, and Phase Transitions

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

10.1: Bulk Properties of Liquids - Molecular Interpretation
10.2: Intermolecular Forces - Origins in Molecular Structure
10.3: Intermolecular Forces in Liquids
10.4: Phase Equilibrium
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10.1: Bulk Properties of Liquids - Molecular Interpretation

Learning Objectives

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

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

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

Surface Tension

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

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

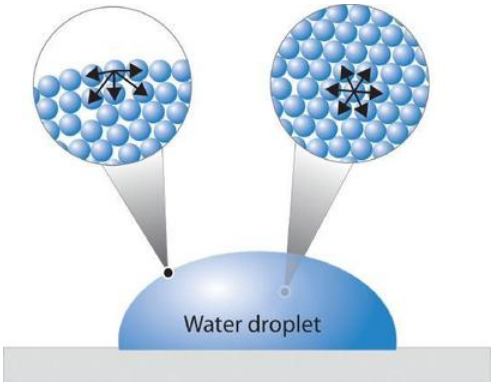


Figure 10.1.1: A Representation of Surface Tension in a Liquid. Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces. (CC BY-SA-NC; anonymous)

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it "floats," even though steel is much denser

than water. Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking. This is better demonstrated in the zero-gravity conditions of space (Figure 10.1.2).



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

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

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

Substance	Surface Tension ($\times 10^{-3}$ 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	—
20°C	72.8	1.00	17.5	—
60°C	66.2	0.47	149	—
100°C	58.9	0.28	760	—

Adding soaps and detergents that disrupt the intermolecular attractions between adjacent water molecules can reduce the surface tension of water. Because they affect the surface properties of a liquid, soaps and detergents are called surface-active agents, or

surfactants. In the 1960s, US Navy researchers developed a method of fighting fires aboard aircraft carriers using “foams,” which are aqueous solutions of fluorinated surfactants. The surfactants reduce the surface tension of water below that of fuel, so the fluorinated solution is able to spread across the burning surface and extinguish the fire. Such foams are now used universally to fight large-scale fires of organic liquids.

Surface Energies and Surface Tension

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

Capillary Action

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

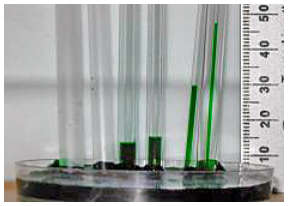


Figure 10.1.3: The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters. (Dr. Clay Robinson, PhD, West Texas A&M University)

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

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

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

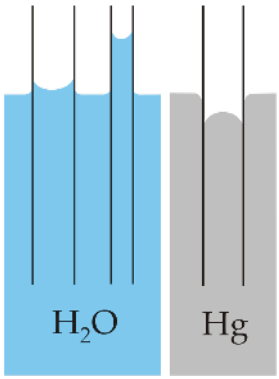


Figure 10.1.4: The Phenomenon of Capillary Action. Capillary action of water compared to mercury, in each case with respect to a polar surface such as glass. (a) This drawing illustrates the shape of the meniscus and the relative height of a mercury column when a glass capillary is put into liquid mercury.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

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

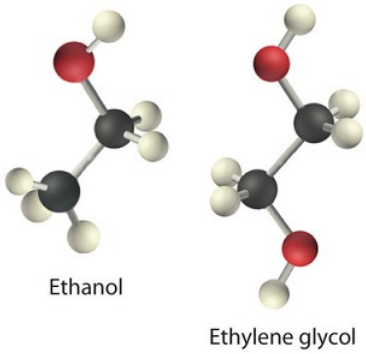
> *Polar substances are drawn up a glass capillary and generally have concave meniscuses and nonpolar substances general avoid the capillary and exhibit convex meniscuses.*

Viscosity

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

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

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



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

There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for

them to become “tangled” with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

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

Application: Motor Oils

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



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

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

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

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

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

Example 10.1.1

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

Given: substance and composition of the glass surface

Asked for: behavior of oil and the shape of meniscus

Strategy:

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

Solution:

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

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

Exercise 10.1.1

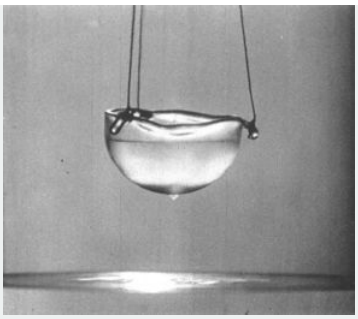
Predict what will happen when a glass capillary is put into a beaker of ethylene glycol. Will the ethylene glycol be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)?

Answer

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

Oddity of Science: Superfluid Helium-4

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



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

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

Boiling Points

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

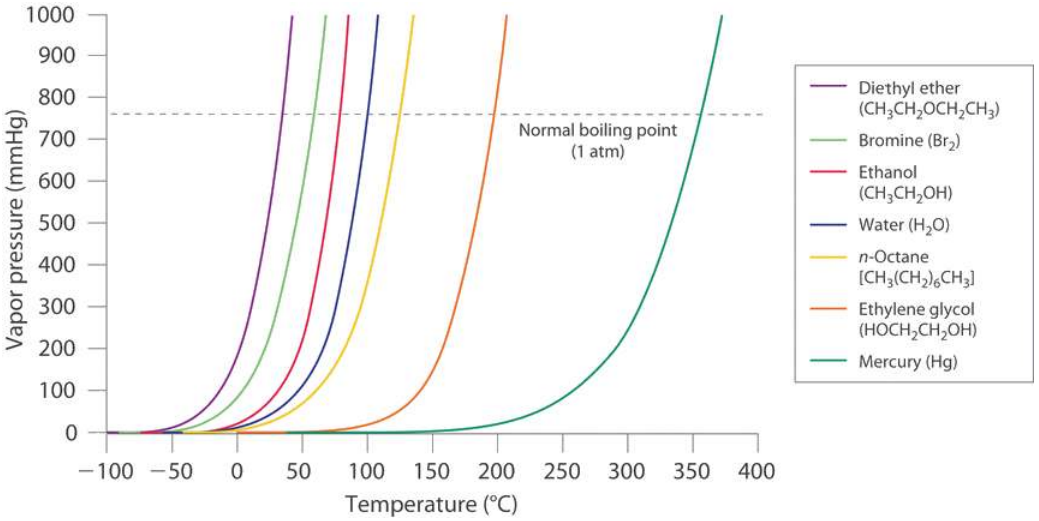


Figure 10.1.8: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC; anonymous)

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

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

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

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

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

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

Example 10.1.2: Boiling Mercury

Use Figure 10.1.8 to estimate the following.

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



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

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

Asked for: corresponding boiling point and pressure

Strategy:

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

Solution:

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

? Exercise 10.1.2: Boiling Ethylene Glycol

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

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

Answer a

200°C

Answer b

450 mmHg

Summary

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

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

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10.2: Intermolecular Forces - Origins in Molecular Structure

Learning Objectives

- To describe the intermolecular forces in liquids.

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

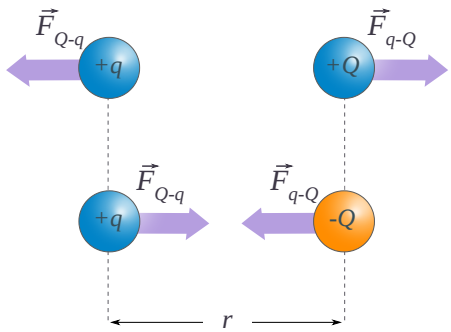
The properties of liquids are intermediate between those of gases and solids but are more similar to solids.

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

Coulombic Interactions

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

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



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

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

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

In this mathematical representation of Coulomb's observations,

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

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

Ion–Ion Interactions

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

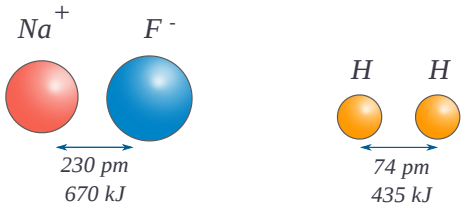


Figure 10.2.1: Ion-Ion attraction in NaF (left) exceeds the covalent bond energy of $\mathrm{H_2}$ (right). (CC BY-NC; Ümit Kaya)

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

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

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

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

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

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

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

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

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

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

Example 10.2.1

When sodium chloride is melted, some of the ion pairs vaporize and form neutral NaCl dimers. How much energy would be released when one mole of 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 10.2.4. 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

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

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.

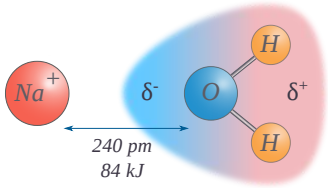


Figure 10.2.3: Ion - Dipole Interaction. (CC BY-NC; Ümit Kaya)

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

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

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

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

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

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

Ion-Ion vs. Ion-Dipole potentials

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

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

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

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

Dipole–Dipole Interactions

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

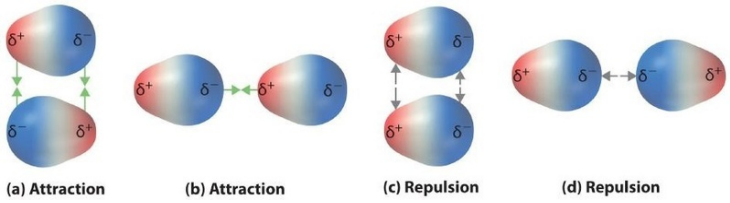


Figure 10.2.5: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or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

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure 10.2.1*c*). Hence dipole–dipole interactions, such as those in Figure 10.2.5*b*, are *attractive intermolecular interactions*, whereas those in Figure 10.2.5*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 10.2.2. On average, however, the attractive interactions dominate.

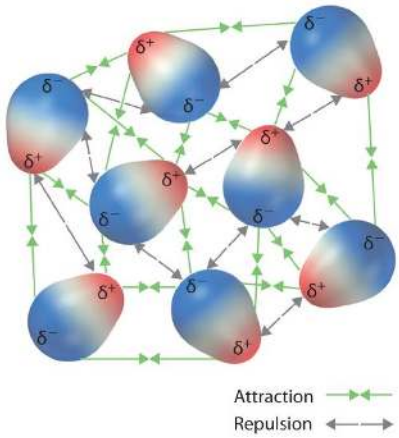


Figure 10.2.6: Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

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

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

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

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

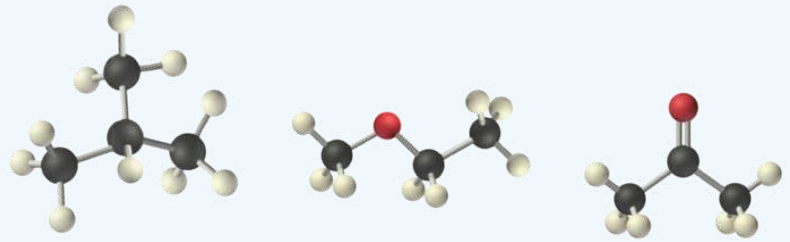
Table 10.2.1: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

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

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

Example 10.2.2

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



Given: compounds

Asked for: order of increasing boiling points

Strategy:

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

Solution:

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

boiling points: 2-methylpropane < ethyl methyl ether < acetone. This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

? Exercise 10.2.1

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

Answer

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

London Dispersion Forces

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

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

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

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

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

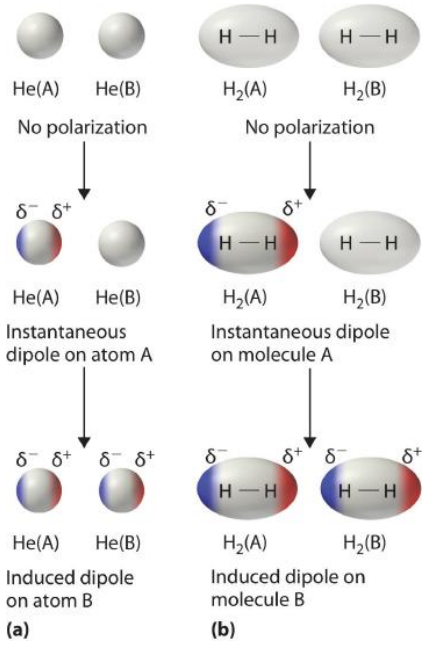


Figure 10.2.3: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

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

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

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

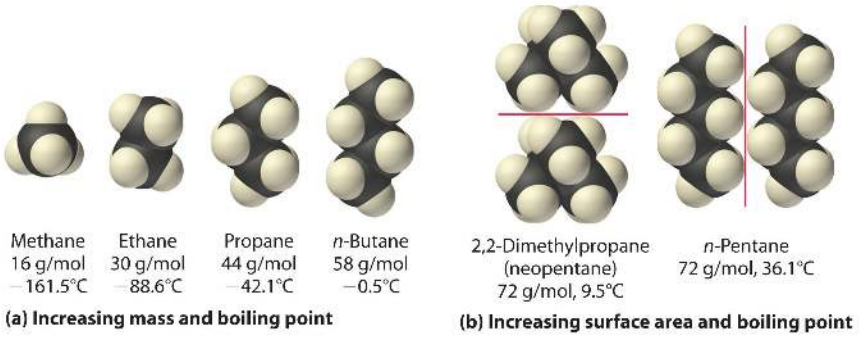


Figure 10.2.4: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface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

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

✔ Example 10.2.2

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

Given: compounds

Asked for: order of increasing boiling points

Strategy:

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

Solution:

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

? Exercise 10.2.2

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

Answer

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

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in

polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed.

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10.3: Intermolecular Forces in Liquids

Learning Objectives

- To describe the intermolecular forces in liquids.

Hydrogen Bonds

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

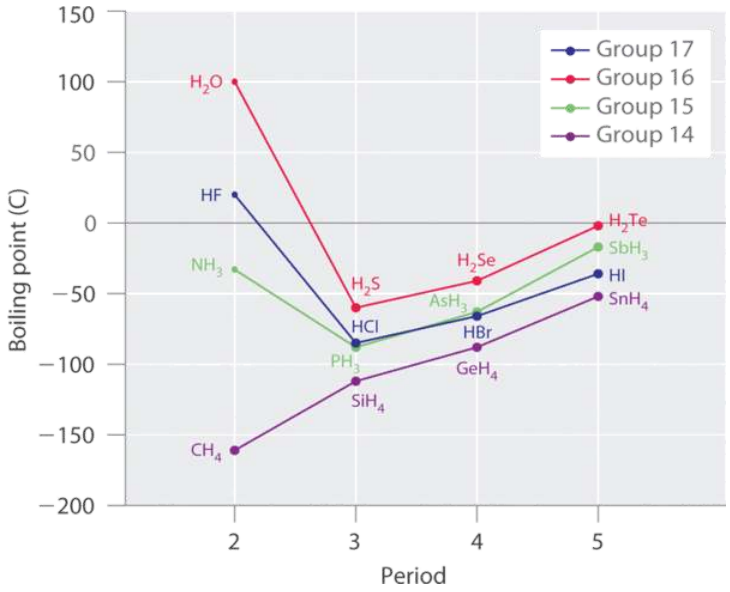


Figure 10.3.1: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously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

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

adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

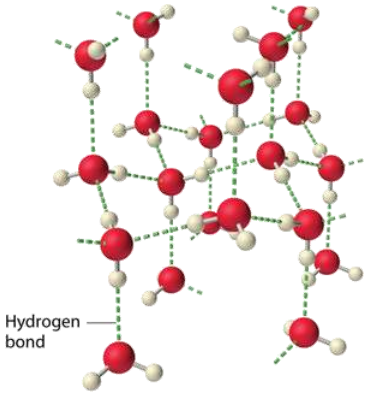


Figure 10.3.2: The Hydrogen-Bonded Structure of Ice

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

It takes two to tango...

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

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

Example 10.3.1

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

Given: compounds

Asked for: formation of hydrogen bonds and structure

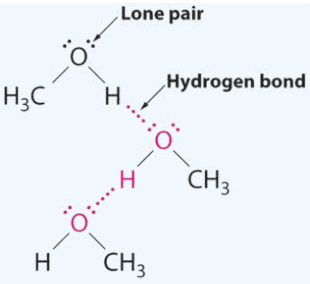
Strategy:

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

Solution:

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

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



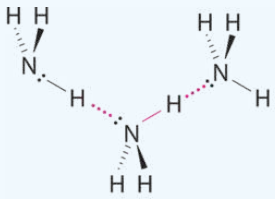
Hydrogen bonding in methanol

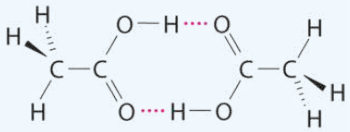
Exercise 10.3.1

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

Answer

CH_3CO_2H and NH_3;


Hydrogen bonding in ammonia


Hydrogen bonding in acetic acid

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

Example 10.3.2

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


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

Given: compounds

Asked for: order of increasing boiling points

Strategy:

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

Solution:

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability

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

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

Exercise 10.3.2

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

Answer

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

Special Properties of Water

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

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

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

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

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



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

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

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O···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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10.4: Phase Equilibrium

Learning Objectives

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

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

Evaporation and Condensation

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

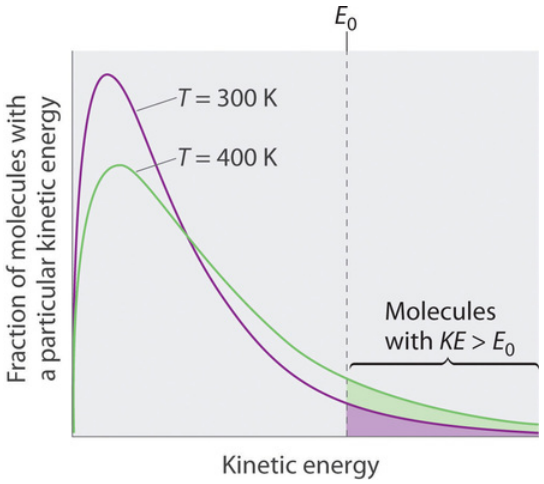


Figure 10.4.1: The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures. Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter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

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

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

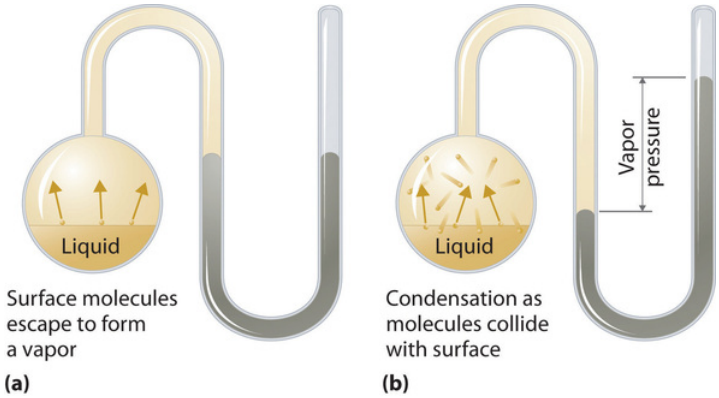


Figure 10.4.2: Vapor Pressure. (a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature,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

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

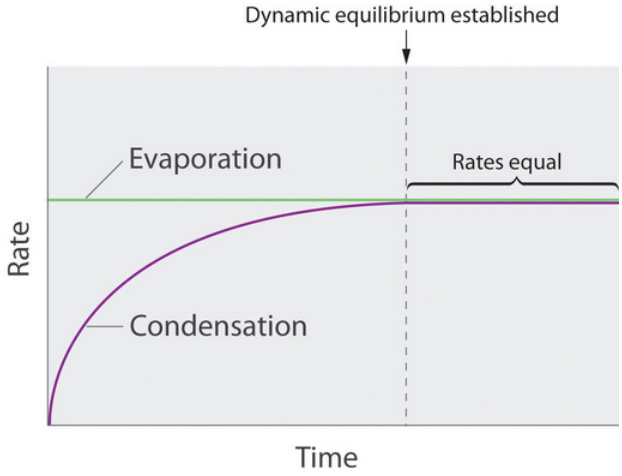


Figure 10.4.3: The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber. The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in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

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

Equilibrium Vapor Pressure

Two opposing processes (such as evaporation and condensation) that occur at the same rate and thus produce no *net* change in a system, constitute a dynamic equilibrium. In the case of a liquid enclosed in a chamber, the molecules continuously evaporate and

condense, but the amounts of liquid and vapor do not change with time. The pressure exerted by a vapor in dynamic equilibrium with a liquid is the equilibrium vapor pressure of the liquid.

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

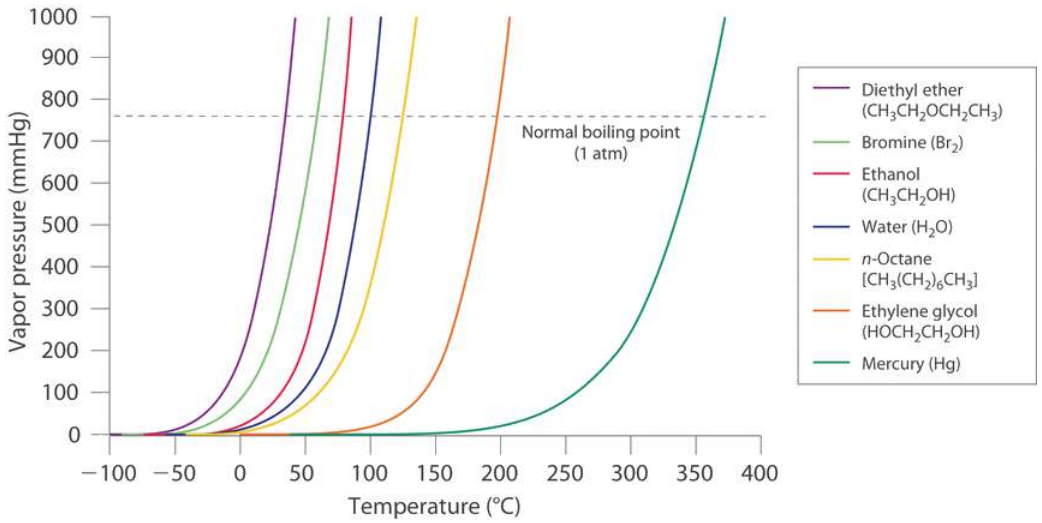


Figure 10.4.4: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC; Anonymous by request)

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

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



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

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

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

where

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

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

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

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



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

Example 10.4.1: Vapor Pressure of Mercury

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

experimentally measured vapor pressures of liquid Hg at four temperatures

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

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

Given: vapor pressures at four temperatures

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

Strategy:

A. Use Equation 10.4.2 to obtain ΔH_{vap} directly from two pairs of values in the table, making sure to convert all values to the appropriate units.

B. Substitute the calculated value of ΔH_{vap} into Equation 10.4.2 to obtain the unknown pressure (P_2).

Solution:

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

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

$$\ln(8.398) = \frac{-\Delta H_{vap}}{8.314\ J/mol\cdot\ \cancel{K}}\left(-2.88\times10^{-4}\ \cancel{K^{-1}}\right)$$

$$2.13 = -\Delta H_{vap}\left(-3.46\times10^{-4}\right) J^{-1}\cdot mol$$

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

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 10.4.1: Vapor Pressure of Nickel

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

Answer

1896°C

Boiling Points

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

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

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

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

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

✓ Example 10.4.2: Boiling Mercury

Use Figure 10.4.4 to estimate the following.

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



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

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

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure 10.4.4 and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.

B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

a. **A** The vapor pressure curve of water intersects the P = 1000 mmHg line at about 110°C; this is therefore the boiling point of water at 1000 mmHg.

b. **B** The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx 75$ mmHg. Hence this is the pressure required for mercury to boil at 250°C.

? Exercise 10.4.2: Boiling Ethlyene Glycol

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

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

Answer a

200°C

Answer b

450 mmHg

Summary

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

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10.5: Phase Transitions

Learning Objectives

- To calculate the energy changes that accompany phase changes.

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

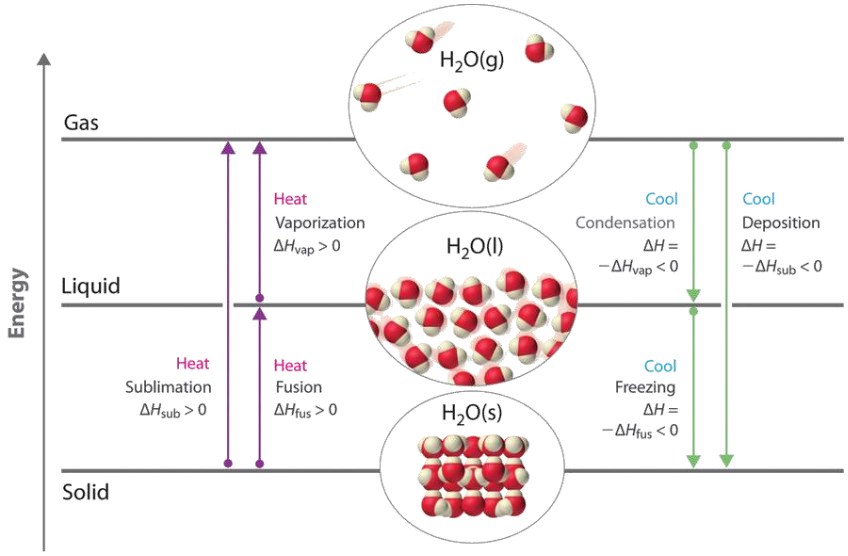


Figure 10.5.1: Enthalpy changes that accompany phase transitions are indicated by purple and green arrows. Purple arrows indicate heating from solid to gas, solid to liquid, and liquid to gas. Green arrows indicate cooling from gas to solid, gas to liquid, and liquid to solid. (CC BY-SA-NC; anoymous)

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 10.5.1.

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

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

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

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)

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

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

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



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

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

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

Fusion, vaporization, and sublimation are endothermic processes; they occur only with the absorption of heat. Anyone who has ever stepped out of a swimming pool on a cool, breezy day has felt the heat loss that accompanies the evaporation of water from the skin. Our bodies use this same phenomenon to maintain a constant temperature: we perspire continuously, even when at rest, losing about 600 mL of water daily by evaporation from the skin. We also lose about 400 mL of water as water vapor in the air we exhale, which also contributes to cooling. Refrigerators and air-conditioners operate on a similar principle: heat is absorbed from the object or area to be cooled and used to vaporize a low-boiling-point liquid, such as ammonia or the chlorofluorocarbons (CFCs)

and the hydrofluorocarbons (HCFCs). The vapor is then transported to a different location and compressed, thus releasing and dissipating the heat. Likewise, ice cubes efficiently cool a drink not because of their low temperature but because heat is required to convert ice at 0°C to liquid water at 0°C.

Temperature Curves

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

Heating Curves

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

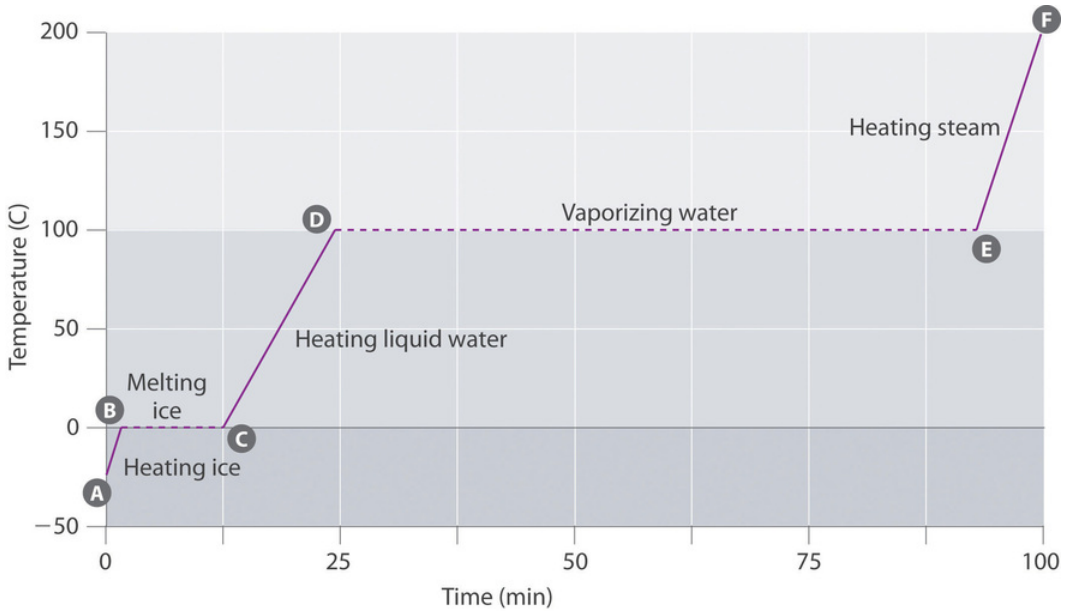


Figure 10.5.3: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and −23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

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

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

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

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

Cooling Curves

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

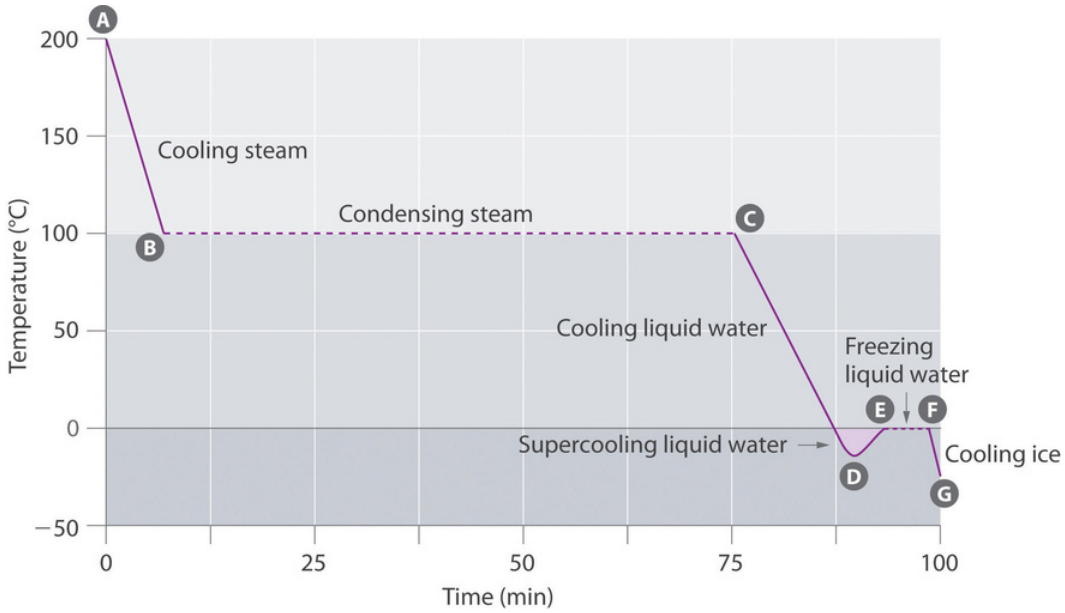


Figure 10.5.4: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid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

Supercooling effects have a huge impact on Earth's climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about −10°C, rather than freezing into ice crystals that

are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimes, it absorbs heat from the cloud, often with the desired results.



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

Example 10.5.1: Cooling Tea

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

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

Asked for: final temperature

Strategy

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

Solution

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

$$q = mC_s\Delta T$$

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

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

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

For our 50.0 g ice cube:

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

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

$$q_{tea} = -16,700J = 500mL \cdot \frac{1.00\ g}{1\ mL} \cdot 4.184J/(g \bullet {}^\circ C)\Delta T$$
$$\Delta T = -7.98\,{}^\circ C = T_f - T_i$$
$$= 12.02\,{}^\circ C$$

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

$$q_{ice} = -q_{tea}$$
$$q_{ice} = m_{ice}C_s\Delta T = 50.0g \cdot 4.184J/(g \bullet {}^\circ C) \cdot (T_f - 0.0\,{}^\circ C)$$
$$= 209.2J/{}^\circ C \cdot T_f$$
$$q_{tea} = m_{tea}C_s\Delta T = 500g \cdot 4.184J/(g \bullet {}^\circ C) \cdot (T_f - 12.02\,{}^\circ C) = 2092J/{}^\circ C \cdot T_f - 25,150J$$
$$209.2J/{}^\circ C \cdot T_f = -2092J/{}^\circ C \cdot T_f + 25,150J$$
$$2301.2J/{}^\circ C \cdot T_f = 25,150J$$
$$T_f = 10.9\,{}^\circ C$$

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

? Exercise 10.5.1: Death by Freezing

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

Answer

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

Summary

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

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

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10.6: Phase Diagrams

Learning Objectives

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

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

Introduction

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

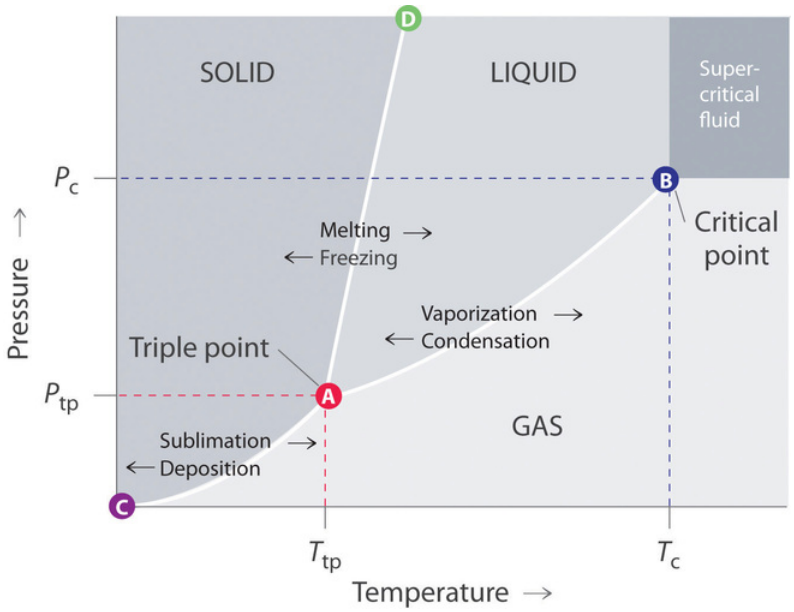


Figure 10.6.1: A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region

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

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

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

The Phase Diagram of Water

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

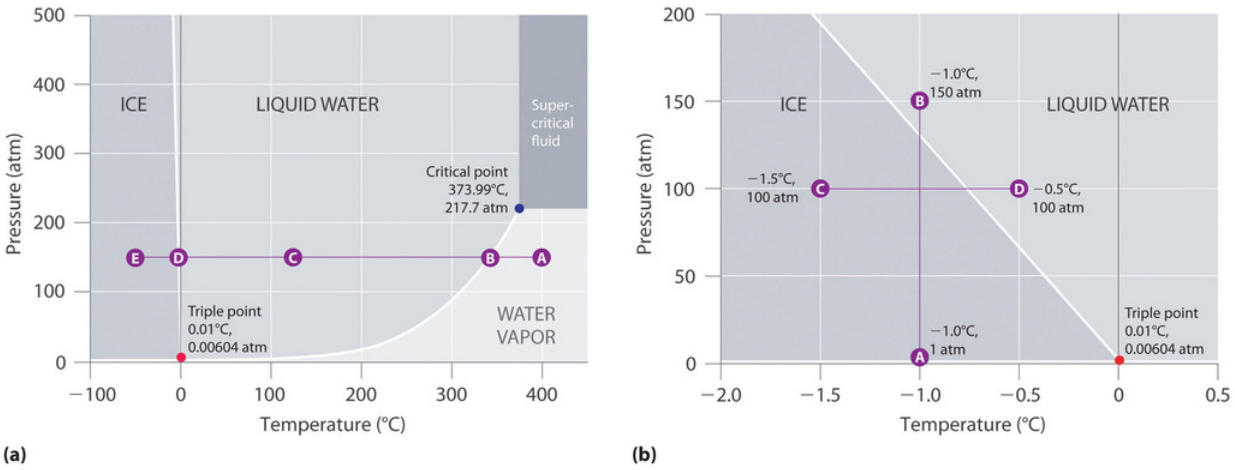


Figure 10.6.2: Two Versions of the Phase Diagram of Water. (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters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

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

In Figure 10.6.2*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 10.6.1: Water

Referring to the phase diagram of water in Figure 10.6.2

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

Given: phase diagram, temperature, and pressure

Asked for: physical form and physical changes

Strategy:

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

Solution:

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

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

? Exercise 10.6.2

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

Answer

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

The Phase Diagram of Carbon Dioxide

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



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

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

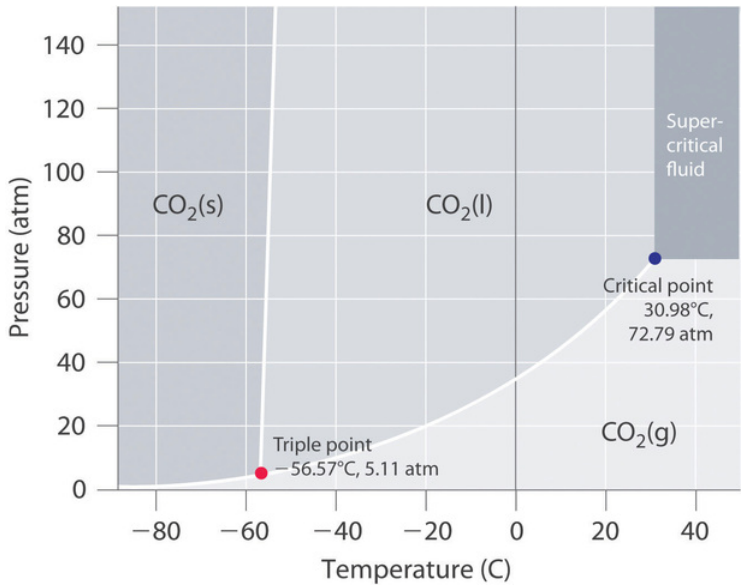


Figure 10.6.3: The Phase Diagram of Carbon Dioxide. Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

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

The Critical Point

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

Figure 10.6.1: Critical Temperatures and Pressures of Some Simple Substances

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

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



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

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

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

Q.1

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

Solution

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

Q.3

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

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

Solution

We need to compute the density of the liquid first:

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

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:

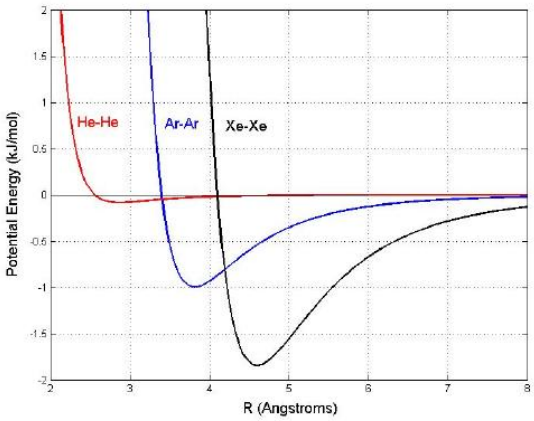
a. fluoride ion
b. a molecule of hydrogen fluoride
c. atom of Argon

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

https://chem.libretexts.org/@go/page/531540

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

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

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

Q.23

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

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

Solution

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

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

Q.24

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

Solution

The primary intermolecular forces in the compounds are

- HF → 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.

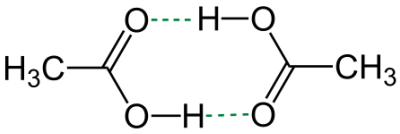
Solution

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

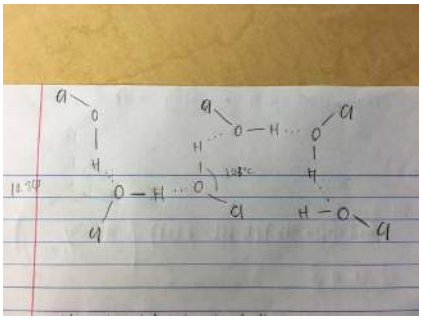


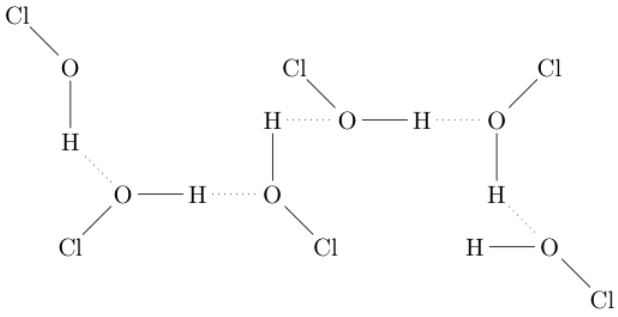
The diagram above shows a reasonable structure of a acetic acid dimer, where the dash lines represent hydrogen bonds.

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^oC) compared to the other hydrogen halides. This is because HF is capable of forming hydrogen bonding within its compounds.

Solution

https://chem.libretexts.org/@go/page/531540

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

Q.31

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

Solution

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

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

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

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

Standard pressure = 1 atm

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

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

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

Q.35

Consider the reaction at 25ºC.

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

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

Solution

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

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

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

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

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

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

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

Solution

At $20.0^\circ C$, water H_2O has a greater surface tension ($72.86\frac{mN}{m}$) than benzene, (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

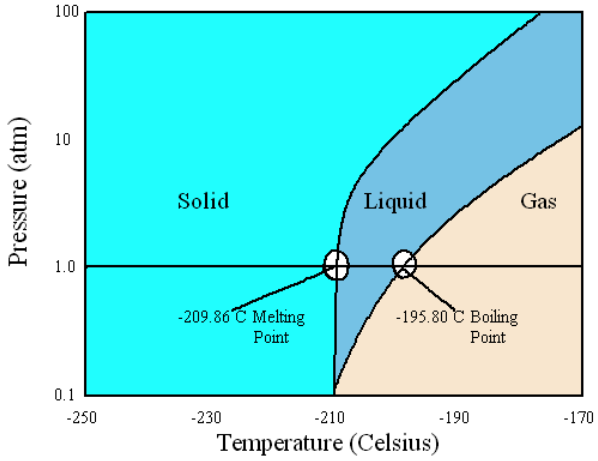
Compression favors the denser phase. Since Ga is a solid at $301.9K$, then it will undergo a phase change to become a liquid.

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

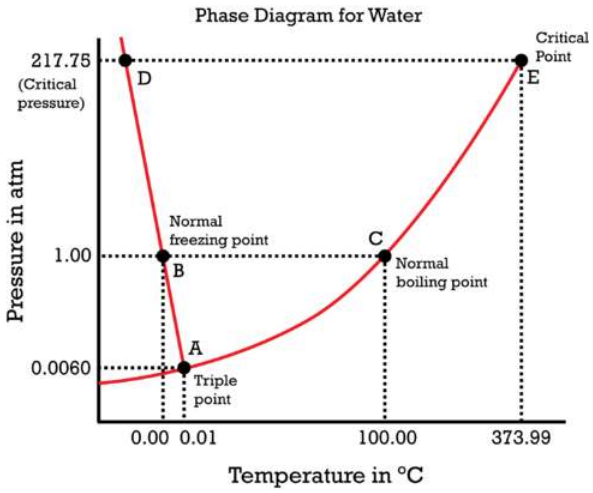


Figure used with permission (CK-12 Foundation – Christopher Auyeung)

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

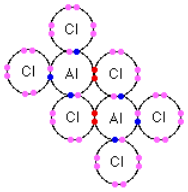
The melting points of the chlorides of third period elements are: $NaCl = 1074\,K$, $MgCl_2 = 987\,K$, $AlCl_3 = 465\,K$, $SiCl_4 = 204.4\,K$, $PCl_3 = 179\,K$. Based on the applicable intermolecular forces present in each compound, explain this trend in melting points.

Solution

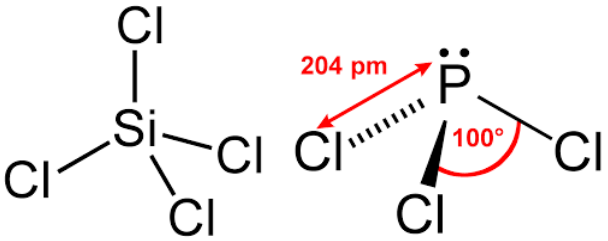
Experimentally, as the chloride compounds make their way across the third period elements, the melting points gradually decrease. This may appear an easy question to address since the melting points are a also measure of the magnitude of the intermolecular forces as play in the specific system, however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

Both ($NaCl$ and $MgCl_2$) are both "ionic solids" with strong ion-ion bonding and hence have the highest melting temperatures in the comparative series. We would expect the Na^+ ions in ($NaCl$ to have weaker Coulombic interactions than the Mg^{2+} ions in $MgCl_2$ 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 $MgCl_2$ are 876 and 2526 kJ/mol). However, this ionic perspective is insufficient to explain the observed melting points with ($NaCl > MgCl_2$), 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 $Na-Cl$ bond is 71% and for $Mg-Cl$ is even lower, at 58%. Hence, the $Na-Cl$ bond is 29% covalent and the $Mg-Cl$ bond is 42% covalent. The covalent character reduces the melting point of $MgCl_2$, even though Mg^+ has a higher charge-to-size ratio than Na^+.

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



Both $SiCl_4$ and 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.



$SiCl_4$ is a tetrahedral molecule with no dipole moment (nor quadrupole moment either). 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 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 PCl_4, which beats out the weak dipole-dipole interactions in PCl_4.

Q.71

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

Solution

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

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

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CHAPTER OVERVIEW

11: Solutions

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

Template:HideTOC

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

11.1: Composition of Solutions
11.2: Nature of Dissolved Species
11.3: Reaction Stoichiometry in Solutions- Acid-Base Titrations
11.4: Reaction Stoichiometry in Solutions- Oxidation-Reduction Titrations
11.5: Phase Equilibrium in Solutions - Nonvolatile Solutes
11.6: Phase Equilibrium in Solutions - Volatile Solutes
11.7: Colloidal Suspensions
11.E: Solutions (Exercises)

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11.1: Composition of Solutions

Learning Objectives

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

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

Example 11.1.1: Molarity and Mole Fraction

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

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

Given: mass of substance and mass and density of solution

Asked for: molarity and mole fraction

Strategy:

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

Solution:

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

$$\text{moles } CH_3CO_2H = \frac{3.78 \text{ g } CH_3CO_2H}{60.05 \text{ g/mol}}$$

$$= 0.0629 \text{ mol}$$

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

$$\text{volume} = \frac{\text{mass}}{\text{density}}$$

$$= \frac{100.0 \text{ g solution}}{1.00 \text{ g/mL}} = 100 \text{ } mL$$

Then calculate the molarity directly.

$$\text{molarity of } CH_3CO_2H = \frac{\text{moles } CH_3CO_2H}{\text{liter solution}}$$

$$= \frac{0.0629 \text{ } mol \text{ } CH_3CO_2H}{(100 \text{ mL})(1 \text{ } L/1000 \text{ mL})} = 0.629 \text{ } M \text{ } CH_3CO_2H$$

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

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

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

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

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

? Exercise 11.1.1: Molarity and Mole Fraction

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

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

Answer a

6.10 M HCl

Answer b

$\chi_{HCl} = 0.111$

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

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

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

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

$$\text{mass percentage} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100 \tag{11.1.2}$$

$$\text{parts per million (ppm)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \tag{11.1.3}$$

$$\text{parts per billion (ppb)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9 \tag{11.1.4}$$

In the health sciences, the concentration of a solution is often expressed as parts per thousand (ppt), indicated as a proportion. For example, adrenalin, the hormone produced in high-stress situations, is available in a 1:1000 solution, or one gram of adrenalin per

1000 g of solution.

The labels on bottles of commercial reagents often describe the contents in terms of mass percentage. Sulfuric acid, for example, is sold as a 95% aqueous solution, or 95 g of H_2SO_4 per 100 g of solution. Parts per million and parts per billion are used to describe concentrations of highly dilute solutions. These measurements correspond to milligrams and micrograms of solute per kilogram of solution, respectively. For dilute aqueous solutions, this is equal to milligrams and micrograms of solute per liter of solution (assuming a density of 1.0 g/mL).

✔ Example 11.1.2: Molarity and Mass

Several years ago, millions of bottles of mineral water were contaminated with benzene at ppm levels. This incident received a great deal of attention because the lethal concentration of benzene in rats is 3.8 ppm. A 250 mL sample of mineral water has 12.7 ppm of benzene. Because the contaminated mineral water is a very dilute aqueous solution, we can assume that its density is approximately 1.00 g/mL.

a. What is the molarity of the solution?
b. What is the mass of benzene in the sample?

Given: volume of sample, solute concentration, and density of solution

Asked for: molarity of solute and mass of solute in 250 mL

Strategy:

A. Use the concentration of the solute in parts per million to calculate the molarity.
B. Use the concentration of the solute in parts per million to calculate the mass of the solute in the specified volume of solution.

Solution:

a. A To calculate the molarity of benzene, we need to determine the number of moles of benzene in 1 L of solution. We know that the solution contains 12.7 ppm of benzene. Because 12.7 ppm is equivalent to 12.7 mg/1000 g of solution and the density of the solution is 1.00 g/mL, the solution contains 12.7 mg of benzene per liter (1000 mL). The molarity is therefore

$$\begin{aligned}\text{molarity} &= \frac{\text{moles}}{\text{liter solution}} \\ &= \frac{(12.7\ \cancel{mg})\left(\frac{1\ g}{1000\ \cancel{mg}}\right)\left(\frac{1\ mol}{78.114\ \cancel{g}}\right)}{1.00\ L} \\ &= 1.63 \times 10^{-4} M\end{aligned}$$

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

$$\begin{aligned}\text{mass of benzene} &= \frac{(12.7\ mg\ \text{benzene})(250\ \cancel{mL})}{1000\ \cancel{mL}} \\ &= 3.18\ mg \\ &= 3.18 \times 10^{-3}\ g\ \text{benzene}\end{aligned}$$

? Exercise 11.1.2: Molarity of Lead Solution

The maximum allowable concentration of lead in drinking water is 9.0 ppb.

a. What is the molarity of Pb^{2+} in a 9.0 ppb aqueous solution?
b. Use your calculated concentration to determine how many grams of Pb^{2+} are in an 8 oz glass of water.

Answer a

4.3×10^{-8} M

Answer b

2×10^{-6} g

How do chemists decide which units of concentration to use for a particular application? Although molarity is commonly used to express concentrations for reactions in solution or for titrations, it does have one drawback—molarity is the number of moles of solute divided by the volume of the solution, and the volume of a solution depends on its density, which is a function of temperature. Because volumetric glassware is calibrated at a particular temperature, typically 20°C, the molarity may differ from the original value by several percent if a solution is prepared or used at a significantly different temperature, such as 40°C or 0°C. For many applications this may not be a problem, but for precise work these errors can become important. In contrast, mole fraction, molality, and mass percentage depend on only the masses of the solute and solvent, which are independent of temperature.

Mole fraction is not very useful for experiments that involve quantitative reactions, but it is convenient for calculating the partial pressure of gases in mixtures, as discussed previously. Mole fractions are also useful for calculating the vapor pressures of certain types of solutions. Molality is particularly useful for determining how properties such as the freezing or boiling point of a solution vary with solute concentration. Because mass percentage and parts per million or billion are simply different ways of expressing the ratio of the mass of a solute to the mass of the solution, they enable us to express the concentration of a substance even when the molecular mass of the substance is unknown. Units of ppb or ppm are also used to express very low concentrations, such as those of residual impurities in foods or of pollutants in environmental studies.

Table 11.1.1 summarizes the different units of concentration and typical applications for each. When the molar mass of the solute and the density of the solution are known, it becomes relatively easy with practice to convert among the units of concentration we have discussed, as illustrated in Example 11.1.3.

Table 11.1.1: Different Units for Expressing the Concentrations of Solutions*

Unit	Definition	Application
molarity (M)	moles of solute/liter of solution (mol/L)	Used for quantitative reactions in solution and titrations; mass and molecular mass of solute and volume of solution are known.
mole fraction (χ)	moles of solute/total moles present (mol/mol)	Used for partial pressures of gases and vapor pressures of some solutions; mass and molecular mass of each component are known.
molality (m)	moles of solute/kg of solvent (mol/kg)	Used in determining how colligative properties vary with solute concentration; masses and molecular mass of solute are known.
mass percentage (%)	[mass of solute (g)/mass of solution (g)] × 100	Useful when masses are known but molecular masses are unknown.
parts per thousand (ppt)	[mass of solute/mass of solution] × 10^3 (g solute/kg solution)	Used in the health sciences, ratio solutions are typically expressed as a proportion, such as 1:1000.
parts per million (ppm)	[mass of solute/mass of solution] × 10^6 (mg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.
parts per billion (ppb)	[mass of solute/mass of solution] × 10^9 (µg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.

*The molarity of a solution is temperature dependent, but the other units shown in this table are independent of temperature.

Example 11.1.3: Vodka

Vodka is essentially a solution of ethanol in water. Typical vodka is sold as "80 proof," which means that it contains 40.0% ethanol by volume. The density of pure ethanol is 0.789 g/mL at 20°C. If we assume that the volume of the solution is the sum of the volumes of the components (which is not strictly correct), calculate the following for the ethanol in 80-proof vodka.

a. the mass percentage
b. the mole fraction
c. the molarity
d. the molality

Given: volume percent and density

Asked for: mass percentage, mole fraction, molarity, and molality

Strategy:

A. Use the density of the solute to calculate the mass of the solute in 100.0 mL of solution. Calculate the mass of water in 100.0 mL of solution.
B. Determine the mass percentage of solute by dividing the mass of ethanol by the mass of the solution and multiplying by 100.
C. Convert grams of solute and solvent to moles of solute and solvent. Calculate the mole fraction of solute by dividing the moles of solute by the total number of moles of substances present in solution.
D. Calculate the molarity of the solution: moles of solute per liter of solution. Determine the molality of the solution by dividing the number of moles of solute by the kilograms of solvent.

Solution:

The key to this problem is to use the density of pure ethanol to determine the mass of ethanol (CH_3CH_2OH), abbreviated as EtOH, in a given volume of solution. We can then calculate the number of moles of ethanol and the concentration of ethanol in any of the required units. A Because we are given a percentage by volume, we assume that we have 100.0 mL of solution. The volume of ethanol will thus be 40.0% of 100.0 mL, or 40.0 mL of ethanol, and the volume of water will be 60.0% of 100.0 mL, or 60.0 mL of water. The mass of ethanol is obtained from its density:

$$mass\ of\ EtOH = (40.0\ \cancel{mL}) \left(\frac{0.789\ g}{\cancel{mL}} \right) = 31.6\ g\ EtOH$$

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:

$$\begin{aligned} moles\ CH_3CH_2OH &= (31.6\ \ g\ \cancel{CH_3CH_2OH}) \left(\frac{1\ mol}{46.07\ \ g\ \cancel{CH_3CH_2OH}} \right) \\ &= 0.686\ mol\ CH_3CH_2OH \end{aligned}$$

Similarly, the number of moles of water is

$$moles\ H_2O = (60.0\ \ g\ H_2O)\left(\frac{1\ mol\ H_2O}{18.02\ \ g\ H_2O}\right) = 3.33\ mol\ H_2O$$

The mole fraction of ethanol is thus

$$\chi_{CH_3CH_2OH} = \frac{0.686\ \ mol}{0.686\ \ mol + 3.33\ \ mol} = 0.171$$

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

$$M_{CH_3CH_2OH} = \left(\frac{0.686\ mol}{100\ \ mL}\right)\left(\frac{1000\ \ mL}{L}\right) = 6.86\ M$$

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:

$$m_{CH_3CH_2OH} = \left(\frac{0.686\ mol\ EtOH}{60.0\ \ g\ H_2O}\right)\left(\frac{1000\ \ g}{kg}\right) = \frac{11.4\ mol\ EtOH}{kg\ H_2O} = 11.4\ m$$

? Exercise 11.1.3: Toluene/Benzene Solution

A solution is prepared by mixing 100.0 mL of toluene with 300.0 mL of benzene. The densities of toluene and benzene are 0.867 g/mL and 0.874 g/mL, respectively. Assume that the volume of the solution is the sum of the volumes of the components. Calculate the following for toluene.

a. mass percentage
b. mole fraction
c. molarity
d. molality

Answer a

mass percentage toluene = 24.8%

Answer b

$\chi_{toluene} = 0.219$

Answer c

2.35 M toluene

Answer d

3.59 m toluene



A Video Discussing Different Measures of Concentration. Video Link: Measures of Concentration, YouTube (opens in new window) [youtu.be]



A Video Discussing how to Convert Measures of Concentration. Video Link: Converting Units of Concentration, YouTube(opens in new window) [youtu.be]

Summary

Different units are used to express the concentrations of a solution depending on the application. The concentration of a solution is the quantity of solute in a given quantity of solution. It can be expressed in several ways: molarity (moles of solute per liter of solution); mole fraction, the ratio of the number of moles of solute to the total number of moles of substances present; mass percentage, the ratio of the mass of the solute to the mass of the solution times 100; parts per thousand (ppt), grams of solute per kilogram of solution; parts per million (ppm), milligrams of solute per kilogram of solution; parts per billion (ppb), micrograms of solute per kilogram of solution; and molality (m), the number of moles of solute per kilogram of solvent.

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- **13.4: Ways of Expressing Concentration** by Anonymous is licensed CC BY-NC-SA 3.0.

11.2: Nature of Dissolved Species

Learning Objectives

- To understand how enthalpy and entropy changes affect solution formation.
- To use the magnitude of the changes in both enthalpy and entropy to predict whether a given solute–solvent combination will spontaneously form a solution.

In all solutions, whether gaseous, liquid, or solid, the substance present in the greatest amount is the solvent, and the substance or substances present in lesser amounts are the solute(s). The solute does not have to be in the same physical state as the solvent, but the physical state of the solvent usually determines the state of the solution. As long as the solute and solvent combine to give a homogeneous solution, the solute is said to be soluble in the solvent. Table 11.2.1 lists some common examples of gaseous, liquid, and solid solutions and identifies the physical states of the solute and solvent in each.

Table 11.2.1: Types of Solutions

Solution	Solute	Solvent	Examples
gas	gas	gas	air, natural gas
liquid	gas	liquid	seltzer water (CO_2 gas in water)
liquid	liquid	liquid	alcoholic beverage (ethanol in water), gasoline
liquid	solid	liquid	tea, salt water
solid	gas	solid	H_2 in Pd (used for H_2 storage)
solid	solid	liquid	mercury in silver or gold (amalgam often used in dentistry)
solid	solid	solid	alloys and other "solid solutions"

Forming a Solution

The formation of a solution from a solute and a solvent is a physical process, not a chemical one. That is, both solute and solvent can be recovered in chemically unchanged forms using appropriate separation methods. For example, solid zinc nitrate dissolves in water to form an aqueous solution of zinc nitrate:

$$\mathrm{Zn(NO_3)_2(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2\,NO_3^-(aq)} \tag{11.2.1}$$

Because $Zn(NO_3)_2$ can be recovered easily by evaporating the water, this is a physical process. In contrast, metallic zinc appears to dissolve in aqueous hydrochloric acid. In fact, the two substances undergo a chemical reaction to form an aqueous solution of zinc chloride with evolution of hydrogen gas:

$$\mathrm{Zn(s) + 2\,H^+(aq) + 2\,Cl^-(aq) \rightarrow Zn^{2+}(aq) + 2\,Cl^-(aq) + H_2(g)} \tag{11.2.2}$$

When the solution evaporates, we do not recover metallic zinc, so we cannot say that metallic zinc is soluble in aqueous hydrochloric acid because it is chemically transformed when it dissolves. The dissolution of a solute in a solvent to form a solution does not involve a chemical transformation (that it is a physical change).

> *Dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.*

Substances that form a single homogeneous phase in all proportions are said to be completely *miscible* in one another. Ethanol and water are miscible, just as mixtures of gases are miscible. If two substances are essentially insoluble in each other, such as oil and water, they are *immiscible*. Examples of gaseous solutions that we have already discussed include Earth's atmosphere.

The Role of Enthalpy in Solution Formation

Energy is required to overcome the intermolecular interactions in a solute, which can be supplied only by the new interactions that occur in the solution, when each solute particle is surrounded by particles of the solvent in a process called solvation (or hydration when the solvent is water). Thus all of the solute–solute interactions and many of the solvent–solvent interactions must be disrupted for a solution to form. In this section, we describe the role of enthalpy in this process.

Because enthalpy is a state function, we can use a thermochemical cycle to analyze the energetics of solution formation. The process occurs in three discrete steps, indicated by ΔH_1, ΔH_2, and ΔH_3 in Figure 11.2.2 The overall enthalpy change in the formation of the solution (ΔH_{soln}) is the sum of the enthalpy changes in the three steps:

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3 \tag{11.2.3}$$

When a solvent is added to a solution, steps 1 and 2 are both endothermic because energy is required to overcome the intermolecular interactions in the solvent (ΔH_1) and the solute (ΔH_2). Because ΔH is positive for both steps 1 and 2, the solute–solvent interactions (ΔH_3) must be stronger than the solute–solute and solvent–solvent interactions they replace in order for the dissolution process to be exothermic ($\Delta H_{soln} < 0$). When the solute is an ionic solid, ΔH_2 corresponds to the lattice energy that must be overcome to form a solution. The higher the charge of the ions in an ionic solid, the higher the lattice energy. Consequently, solids that have very high lattice energies, such as MgO (−3791 kJ/mol), are generally insoluble in all solvents.

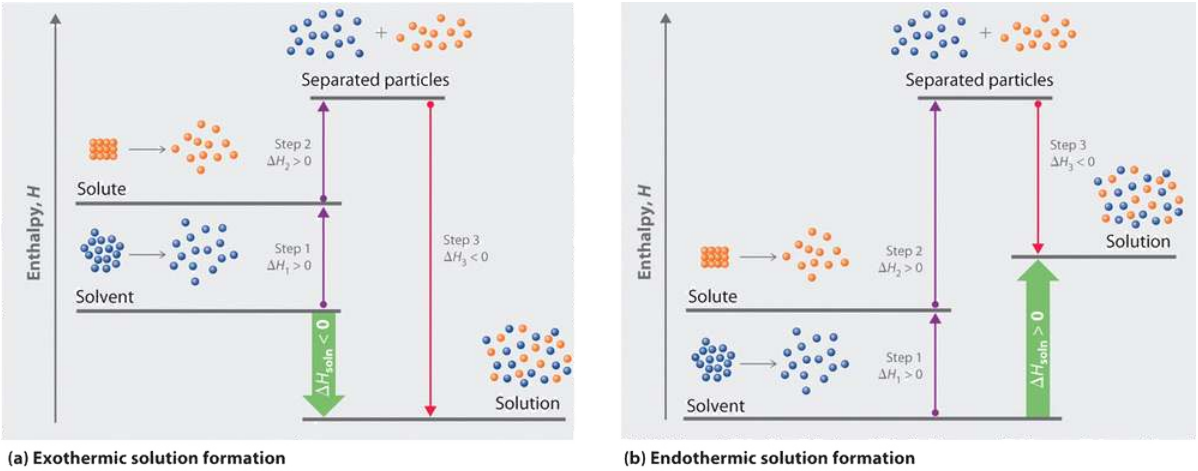


Figure 11.2.2: Enthalpy Changes That Accompany the Formation of a Solution. Solvation can be an exothermic or endothermic process depending on the nature of the solute and solvent. In both cases, step 1, separation of the solvent particles, is energetically uphill ($\Delta H_1 > 0$), as is step 2, separation of the solute particles ($\Delta H_2 > 0$). In contrast, energy is released in step 3 ($\Delta H_3 < 0$) because of interactions between the solute and solvent. (a) When ΔH_3 is larger in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is exothermic ($\Delta H_{soln} < 0$), as shown in the thermochemical cycle. (b) When ΔH_3 is smaller in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is endothermic ($\Delta H_{soln} > 0$).

A positive value for ΔH_{soln} does not mean that a solution will not form. Whether a given process, including formation of a solution, occurs spontaneously depends on whether the total energy of the system is lowered as a result. Enthalpy is only one of the contributing factors. A high ΔH_{soln} is usually an indication that the substance is not very soluble. Instant cold packs used to treat athletic injuries, for example, take advantage of the large positive ΔH_{soln} of ammonium nitrate during dissolution (+25.7 kJ/mol), which produces temperatures less than 0°C (Figure 11.2.3).



Figure 11.2.3: Commercial Cold Packs for Treating Injuries. These packs contain solid NH_4NO_3 and water in separate compartments. When the seal between the compartments is broken, the NH_4NO_3 dissolves in the water. Because ΔH_{soln} for NH_4NO_3 is much greater than zero, heat is absorbed by the cold pack during the dissolution process, producing local temperatures less than 0°C.

Entropy and Solution Formation

The enthalpy change that accompanies a process is important because processes that release substantial amounts of energy tend to occur spontaneously. A second property of any system, its entropy, is also important in helping us determine whether a given process occurs spontaneously. We will discuss entropy in more detail elsewhere, but for now we can state that entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. A perfect crystal at 0 K, whose atoms are regularly arranged in a perfect lattice and are motionless, has an entropy of zero. In contrast, gases have large positive entropies because their molecules are highly disordered and in constant motion at high speeds.

The formation of a solution disperses molecules, atoms, or ions of one kind throughout a second substance, which generally increases the disorder and results in an increase in the entropy of the system. Thus entropic factors almost always favor formation of a solution. In contrast, a change in enthalpy may or may not favor solution formation. The London dispersion forces that hold cyclohexane and n-hexane together in pure liquids, for example, are similar in nature and strength. Consequently, ΔH_{soln} should be approximately zero, as is observed experimentally. Mixing equal amounts of the two liquids, however, produces a solution in which the n-hexane and cyclohexane molecules are uniformly distributed over approximately twice the initial volume. In this case, the driving force for solution formation is not a negative ΔH_{soln} but rather the increase in entropy due to the increased disorder in the mixture. All spontaneous processes with $\Delta H \geq 0$ are characterized by an *increase* in entropy. In other cases, such as mixing oil with water, salt with gasoline, or sugar with hexane, the enthalpy of solution is large and positive, and the increase in entropy resulting from solution formation is not enough to overcome it. Thus in these cases a solution does not form.

> *All spontaneous processes with $\Delta H \geq 0$ are characterized by an increase in entropy.*

Table 11.2.2 summarizes how enthalpic factors affect solution formation for four general cases. The column on the far right uses the relative magnitudes of the enthalpic contributions to predict whether a solution will form from each of the four. Keep in mind that in each case entropy favors solution formation. In two of the cases the enthalpy of solution is expected to be relatively small and can be either positive or negative. Thus the entropic contribution dominates, and we expect a solution to form readily. In the other two cases the enthalpy of solution is expected to be large and positive. The entropic contribution, though favorable, is usually too small to overcome the unfavorable enthalpy term. Hence we expect that a solution will not form readily.

Table 11.2.2: Relative Changes in Enthalpies for Different Solute–Solvent Combinations*

ΔH_1 (separation of solvent molecules)	ΔH_2 (separation of solute particles)	ΔH_3 (solute–solvent interactions)	ΔH_{soln} (ΔH_1 + ΔH_2 +ΔH_3)	Result of Mixing Solute and Solvent†
large; positive	large; positive	large; negative	small; positive or negative	solution will usually form
small; positive	large; positive	small; negative	large; positive	solution will not form
large; positive	small; positive	small; negative	large; positive	solution will not form

ΔH_1 (separation of solvent molecules)	ΔH_2 (separation of solute particles)	ΔH_3 (solute–solvent interactions)	ΔH_{soln} (ΔH_1 + ΔH_2 +ΔH_3)	Result of Mixing Solute and Solvent†
small; positive	small; positive	small; negative	small; positive or negative	solution will usually form

*ΔH_1, ΔH_2, and ΔH_3 refer to the processes indicated in the thermochemical cycle shown in Figure 11.2.2.
†In all four cases, entropy increases.

In contrast to liquid solutions, the intermolecular interactions in gases are weak (they are considered to be nonexistent in ideal gases). Hence mixing gases is usually a thermally neutral process ($\Delta H_{soln} \approx 0$), and the entropic factor due to the increase in disorder is dominant (Figure 11.2.4). Consequently, all gases dissolve readily in one another in all proportions to form solutions.

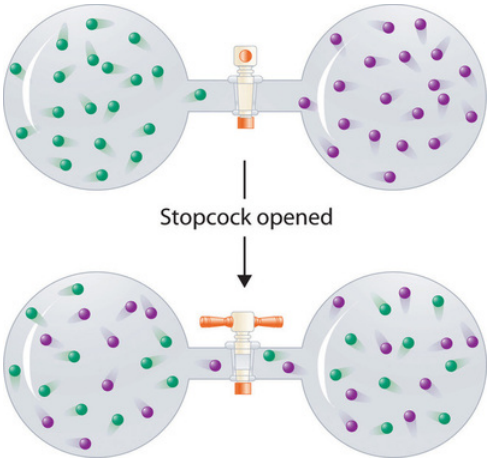
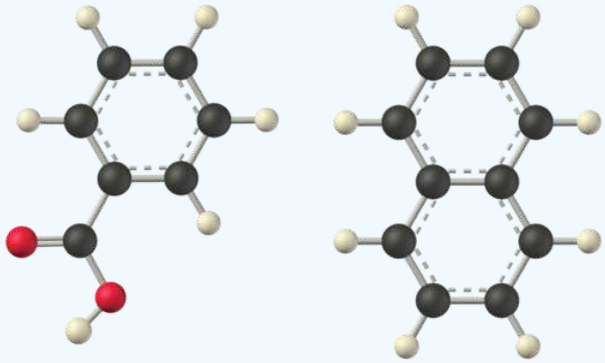


Figure 11.2.4: Formation of a Solution of Two Gases. (top) Pure samples of two different gases are in separate bulbs. (bottom) When the connecting stopcock is opened, diffusion causes the two gases to mix together and form a solution. Even though ΔH_{soln} is zero for the process, the increased entropy of the solution (the increased disorder) versus that of the separate gases favors solution formation.

Example 11.2.1

Considering $LiCl$, benzoic acid ($C_6H_5CO_2H$), and naphthalene, which will be most soluble and which will be least soluble in water?



Given: three compounds

Asked for: relative solubilities in water

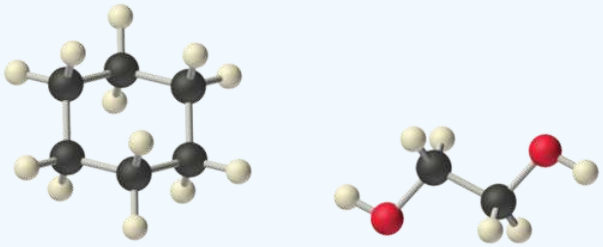
Strategy: Assess the relative magnitude of the enthalpy change for each step in the process shown in Figure 11.2.2 Then use Table 11.2.2to predict the solubility of each compound in water and arrange them in order of decreasing solubility.

Solution:

The first substance, LiCl, is an ionic compound, so a great deal of energy is required to separate its anions and cations and overcome the lattice energy (ΔH_2 is far greater than zero in Equation 11.2.1). Because water is a polar substance, the interactions between both Li^+ and Cl^- ions and water should be favorable and strong. Thus we expect ΔH_3 to be far less than zero, making LiCl soluble in water. In contrast, naphthalene is a nonpolar compound, with only London dispersion forces holding the molecules together in the solid state. We therefore expect ΔH_2 to be small and positive. We also expect the interaction between polar water molecules and nonpolar naphthalene molecules to be weak $\Delta H_3 \approx 0$. Hence we do not expect naphthalene to be very soluble in water, if at all. Benzoic acid has a polar carboxylic acid group and a nonpolar aromatic ring. We therefore expect that the energy required to separate solute molecules (ΔH_2) will be greater than for naphthalene and less than for LiCl. The strength of the interaction of benzoic acid with water should also be intermediate between those of LiCl and naphthalene. Hence benzoic acid is expected to be more soluble in water than naphthalene but less soluble than LiCl. We thus predict LiCl to be the most soluble in water and naphthalene to be the least soluble.

? Exercise 11.2.1

Considering ammonium chloride, cyclohexane, and ethylene glycol ($HOCH_2CH_2OH$), which will be most soluble and which will be least soluble in benzene?



Cyclohexane Ethylene glycol

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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11.3: Reaction Stoichiometry in Solutions- Acid-Base Titrations

Learning Objectives

- Interpret titration curves for strong and weak acid-base systems
- Compute sample pH at important stages of a titration
- Explain the function of acid-base indicators

As seen in the chapter on the stoichiometry of chemical reactions, titrations can be used to quantitatively analyze solutions for their acid or base concentrations. In this section, we will explore the changes in the concentrations of the acidic and basic species present in a solution during the process of a titration.

Titration Curves

Previously, when we studied acid-base reactions in solution, we focused only on the point at which the acid and base were stoichiometrically equivalent. No consideration was given to the pH of the solution before, during, or after the neutralization.

Example 11.3.1: Calculating pH for Titration Solutions: Strong Acid/Strong Base

A titration is carried out for 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* of a strong base NaOH the titration curve is shown in Figure 11.3.1. Calculate the pH at these volumes of added base solution:

a. 0.00 mL
b. 12.50 mL
c. 25.00 mL
d. 37.50 mL

Solution

Since HCl is a strong acid, we can assume that all of it dissociates. The initial concentration of H_3O^+ is $[H_3O^+]_0 = 0.100\ M$. When the base solution is added, it also dissociates completely, providing OH^- ions. The H_3O^+ and OH^- ions neutralize each other, so only those of the two that were in excess remain, and their concentration determines the pH. Thus, the solution is initially acidic (pH < 7), but eventually all the hydronium ions present from the original acid are neutralized, and the solution becomes neutral. As more base is added, the solution turns basic.

The total initial amount of the hydronium ions is:

$$\mathrm{n}(H^+)_0 = [H_3O^+]_0 \times 0.02500\ \mathrm{L} = 0.002500\ \mathrm{mol}$$

Once X mL of the 0.100-*M* base solution is added, the number of moles of the OH^- ions introduced is:

$$\mathrm{n}(OH^-)_0 = 0.100\ M \times \mathrm{X\ mL} \times \left(\frac{1\ \mathrm{L}}{1000\ \mathrm{mL}}\right)$$

The total volume becomes:

$$V = (25.00\ \mathrm{mL} + \mathrm{X\ mL})\left(\frac{1\ \mathrm{L}}{1000\ \mathrm{mL}}\right)$$

The number of moles of H_3O^+ becomes:

$$\mathrm{n}(H^+) = \mathrm{n}(H^+)_0 - \mathrm{n}(OH^-)_0 = 0.002500\ \mathrm{mol} - 0.100\ M \times \mathrm{X\ mL} \times \left(\frac{1\ \mathrm{L}}{1000\ \mathrm{mL}}\right)$$

The concentration of H_3O^+ is:

$$[H_3O^+] = \frac{\mathrm{n}(H^+)}{\mathrm{V}} = \frac{0.002500\ \mathrm{mol} - 0.100\ M \times \mathrm{X\ mL} \times \left(\frac{1\ \mathrm{L}}{1000\ \mathrm{mL}}\right)}{(25.00\ \mathrm{mL} + \mathrm{X\ mL})\left(\frac{1\ \mathrm{L}}{1000\ \mathrm{mL}}\right)}$$

$$= \frac{0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) - 0.100\ M \times \text{X mL}}{25.00 \text{ mL} + \text{X mL}}$$

with the definition of pH:

$$\text{pH} = -\log([\text{H}_3\text{O}^+]) \tag{11.3.1}$$

The preceding calculations work if $\text{n}(\text{H}^+)_0 - \text{n}(\text{OH}^-)_0 > 0$ and so $\text{n}(\text{H}^+) > 0$. When $\text{n}(\text{H}^+)_0 = \text{n}(\text{OH}^-)_0$, the H_3O^+ ions from the acid and the OH^- ions from the base mutually neutralize. At this point, the only hydronium ions left are those from the autoionization of water, and there are no OH^- particles to neutralize them. Therefore, in this case:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-],\ [\text{H}_3\text{O}^+] = K_\text{w} = 1.0 \times 10^{-14};\ [\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}$$

$$\text{pH} = -\log(1.0 \times 10^{-7}) = 7.00$$

Finally, when $\text{n}(\text{OH}^-)_0 > \text{n}(\text{H}^+)_0$, there are not enough H_3O^+ ions to neutralize all the OH^- ions, and instead of $\text{n}(\text{H}^+) = \text{n}(\text{H}^+)_0 - \text{n}(\text{OH}^-)_0$, we calculate: $\text{n}(\text{OH}^-) = \text{n}(\text{OH}^-)_0 - \text{n}(\text{H}^+)_0$

In this case:

$$[\text{OH}^-] = \frac{\text{n}(\text{OH}^-)}{V} = \frac{0.100\ M \times \text{X mL} \times \left(\frac{1 \text{ L}}{1000 \text{ mL}}\right) - 0.002500 \text{ mol}}{(25.00 \text{ mL} + \text{X mL})\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)}$$

$$= \frac{0.100\ M \times \text{X mL} - 0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right)}{25.00 \text{ mL} + \text{X mL}}$$

then using the definition of pOH and its relationship to pH in room temperature aqueous solutios (Equation 11.3.1):

$$\begin{aligned} pH &= 14 - pOH \\ &= 14 + \log([OH^-]) \end{aligned}$$

Let us now consider the four specific cases presented in this problem:

(a) X = 0 mL

$$[\text{H}_3\text{O}^+] = \frac{\text{n}(\text{H}^+)}{V} = \frac{0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right)}{25.00 \text{ mL}} = 0.1\ M$$

then using the definition of pH (Equation 11.3.1):

$$\begin{aligned} pH &= -\log(0.100) \\ &= 1.000 \end{aligned}$$

(b) X = 12.50 mL

$$[\text{H}_3\text{O}^+] = \frac{\text{n}(\text{H}^+)}{V} = \frac{0.002500 \text{ mol} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) - 0.100\ M \times 12.50 \text{ mL}}{25.00 \text{ mL} + 12.50 \text{ mL}} = 0.0333\ M$$

then using the definition of pH (Equation 11.3.1):

$$\begin{aligned} pH &= -\log(0.0333) \\ &= 1.477 \end{aligned}$$

(c) X = 25.00 mL

Since the volumes and concentrations of the acid and base solutions are the same:

$$\text{n}(\text{H}^+)_0 = \text{n}(\text{OH}^-)_0$$

and

$$pH = 7.000$$

as described earlier.

(d) X = 37.50 mL

In this case:

$$\mathrm{n(OH^-)_0 > n(H^+)_0}$$

$$[\mathrm{OH^-}] = \frac{\mathrm{n(OH^-)}}{V} = \frac{0.100\ M \times 35.70\ \mathrm{mL} - 0.002500\ \mathrm{mol} \times \left(\frac{1000\ \mathrm{mL}}{1\ \mathrm{L}}\right)}{25.00\ \mathrm{mL} + 37.50\ \mathrm{mL}} = 0.0200\ M$$

then using the definition of pH (Equation 11.3.1):

$$\begin{aligned}[pH = 14 - pOH \\ &= 14 + \log([OH^-]) \\ &= 14 + \log(0.0200) \\ &= 12.30\end{aligned}$$

Exercise 11.3.1

Calculate the pH for the strong acid/strong base titration between 50.0 mL of 0.100 *M* $HNO_3(aq)$ and 0.200 *M* NaOH (titrant) at the listed volumes of added base:

a. 0.00 mL,
b. 15.0 mL,
c. 25.0 mL, and
d. 40.0 mL.

Answer a

0.00: 1.000

Answer b

15.0: 1.5111

Answer c

25.0: 7e. Do not delete this text first.

Answer d

40.0: 12.523

In Example 11.3.1, we calculated pH at four points during a titration. Table 11.3.1 shows a detailed sequence of changes in the pH of a strong acid and a weak acid in a titration with NaOH.

Table 11.3.1: pH Values in the Titrations of a Strong Acid with a Strong Base and of a Weak Acid with a Strong Base

Volume of 0.100 M NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 M HCl[1]	pH Values 0.100 M CH_3CO_2H[2]
0.0	0.0	1.00	2.87
5.0	0.00050	1.18	4.14
10.0	0.00100	1.37	4.57
15.0	0.00150	1.60	4.92
20.0	0.00200	1.95	5.35

Volume of 0.100 M NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 M HCl[1]	pH Values 0.100 M CH_3CO_2H[2]
22.0	0.00220	2.20	5.61
24.0	0.00240	2.69	6.13
24.5	0.00245	3.00	6.44
24.9	0.00249	3.70	7.14
25.0	0.00250	7.00	8.72
25.1	0.00251	10.30	10.30
25.5	0.00255	11.00	11.00
26.0	0.00260	11.29	11.29
28.0	0.00280	11.75	11.75
30.0	0.00300	11.96	11.96
35.0	0.00350	12.22	12.22
40.0	0.00400	12.36	12.36
45.0	0.00450	12.46	12.46
50.0	0.00500	12.52	12.52

1. Titration of 25.00 mL of 0.100 *M* HCl (0.00250 mol of HCI) with 0.100 *M* NaOH.
2. Titration of 25.00 mL of 0.100 *M* CH_3CO_2H (0.00250 mol of CH_3CO_2H) with 0.100 *M* NaOH.

The simplest acid-base reactions are those of a strong acid with a strong base. Table 11.3.1 shows data for the titration of a 25.0-mL sample of 0.100 *M* hydrochloric acid with 0.100 *M* sodium hydroxide. The values of the pH measured after successive additions of small amounts of NaOH are listed in the first column of this table, and are graphed in Figure 11.3.1, in a form that is called a titration curve. The pH increases slowly at first, increases rapidly in the middle portion of the curve, and then increases slowly again. The point of inflection (located at the midpoint of the vertical part of the curve) is the equivalence point for the titration. It indicates when equivalent quantities of acid and base are present. For the titration of a strong acid with a strong base, the equivalence point occurs at a pH of 7.00 and the points on the titration curve can be calculated using solution stoichiometry (Table 11.3.1 and Figure 11.3.1).

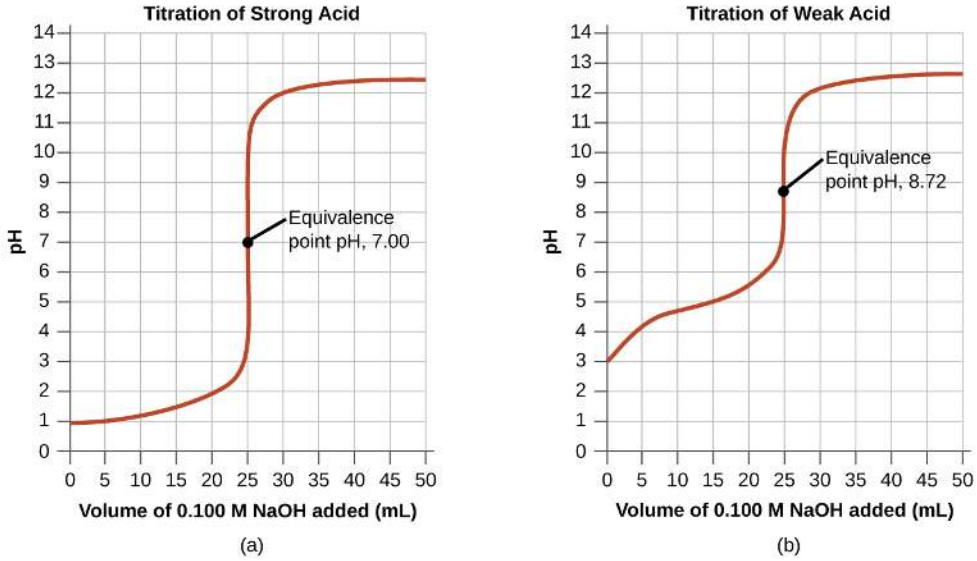


Figure 11.3.1: (a) The titration curve for the titration of 25.00 mL of 0.100 M HCl (strong acid) with 0.100 M NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 M CH_3CO_2H (weak acid) with 0.100 M NaOH (strong base) has an equivalence point of 8.72 pH.

Two graphs are shown. The first graph on the left is titled “Titration of Weak Acid.” The horizontal axis is labeled “Volume of 0.100 M N a O H added (m L).” Markings and vertical gridlines are provided every 5 units from 0 to 50. The vertical axis is labeled “p H” and is marked every 1 unis beginning at 0 extending to 14. A red curve is drawn on the graph which increases steadily from the point (0, 3) up to about (20, 5.5) after which the graph has a vertical section from (25, 7) up to (25, 11). The graph then levels off to a value of about 12.5 from about 40 m L up to 50 m L. The midpoint of the vertical segment of the curve is labeled “Equivalence point p H, 8.72.” The second graph on the right is titled “Titration of Strong Acid.” The horizontal axis is labeled “Volume of 0.100 M N a O H added (m L).” Markings and vertical gridlines are provided every 5 units from 0 to 50. The vertical axis is labeled “p H” and is marked every 1 units beginning at 0 extending to 14. A red curve is drawn on the graph which increases gradually from the point (0, 1) up to about (22.5, 2.2) after which the graph has a vertical section from (25, 4) up to nearly (25, 11). The graph then levels off to a value of about 12.4 from about 40 m L up to 50 m L. The midpoint of the vertical segment of the curve is labeled “Equivalence point p H, 7.00.”

The titration of a weak acid with a strong base (or of a weak base with a strong acid) is somewhat more complicated than that just discussed, but it follows the same general principles. Let us consider the titration of 25.0 mL of 0.100 *M* acetic acid (a weak acid) with 0.100 *M* sodium hydroxide and compare the titration curve with that of the strong acid. Table 11.3.1 gives the pH values during the titration, Figure 11.3.1*b* shows the titration curve.

Although the initial volume and molarity of the acids are the same, there are important differences between the two titration curves. The titration curve for the weak acid begins at a higher value (less acidic) and maintains higher pH values up to the equivalence point. This is because acetic acid is a weak acid, which is only partially ionized. The pH at the equivalence point is also higher (8.72 rather than 7.00) due to the hydrolysis of acetate, a weak base that raises the pH:

$$\mathrm{CH_3CO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2H}(l) + \mathrm{OH^-}(aq)$$

After the equivalence point, the two curves are identical because the pH is dependent on the excess of hydroxide ion in both cases.

Example 11.3.2: Titration of a Weak Acid with a Strong Base

The titration curve shown in Figure 11.3.1*b* is for the titration of 25.00 mL of 0.100 *M* CH_3CO_2H with 0.100 *M* NaOH. The reaction can be represented as:

$$\mathrm{CH_3CO_2H} + \mathrm{OH^-} \longrightarrow \mathrm{CH_3CO_2^-} + \mathrm{H_2O}$$

a. What is the initial pH before any amount of the NaOH solution has been added? $K_a = 1.8 \times 10^{-5}$ for CH_3CO_2H.
b. Find the pH after 25.00 mL of the NaOH solution have been added.
c. Find the pH after 12.50 mL of the NaOH solution has been added.
d. Find the pH after 37.50 mL of the NaOH solution has been added.

Solution

(a) Assuming that the dissociated amount is small compared to 0.100 *M*, we find that:

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} \approx \frac{[H_3O^+]^2}{[CH_3CO_2H]_0}$$

and

$$[H_3O^+] = \sqrt{K_a \times [CH_3CO_2H]} = \sqrt{1.8 \times 10^{-5} \times 0.100} = 1.3 \times 10^{-3}$$

$$pH = -\log(1.3 \times 10^{-3}) = 2.87$$

(b) After 25.00 mL of NaOH are added, the number of moles of NaOH and CH_3CO_2H are equal because the amounts of the solutions and their concentrations are the same. All of the CH_3CO_2H has been converted to $CH_3CO_2^-$. The concentration of the $CH_3CO_2^-$ ion is:

$$\frac{0.00250 \text{ mol}}{0.0500 \text{ L}} = 0.0500 \text{ M} CH_3CO_2^-$$

The equilibrium that must be focused on now is the basicity equilibrium for $CH_3CO_2^-$:

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

so we must determine K_b for the base by using the ion product constant for water:

$$K_b = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2^-]}$$

$$K_a = \frac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]}, \text{ so } \frac{[CH_3CO_2H]}{[CH_3CO_2^-]} = \frac{[H^+]}{K_a}.$$

Since $K_w = [H^+][OH^-]$:

$$K_b = \frac{[H^+][OH^-]}{K_a} \tag{11.3.2}$$

$$= \frac{K_w}{K_a} \tag{11.3.3}$$

$$= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \tag{11.3.4}$$

$$= 5.6 \times 10^{-10} \tag{11.3.5}$$

Let us denote the concentration of each of the products of this reaction, CH_3CO_2H and OH^-, as *x*. Using the assumption that *x* is small compared to 0.0500 *M*, $K_b = \frac{x^2}{0.0500\ M}$, and then:

$$x = [OH^-] = 5.3 \times 10^{-6}$$

$$pOH = -\log(5.3 \times 10^{-6}) = 5.28$$

$$pH = 14.00 - 5.28 = 8.72$$

Note that the pH at the equivalence point of this titration is significantly greater than 7.

(c) In (a), 25.00 mL of the NaOH solution was added, and so practically all the CH_3CO_2H was converted into $CH_3CO_2^-$. In this case, only 12.50 mL of the base solution has been introduced, and so only half of all the CH_3CO_2H is converted into $CH_3CO_2^-$. The total initial number of moles of CH_3CO_2H is 0.02500L × 0.100 $\underline{M}$ = 0.00250 mol, and so after adding the NaOH, the numbers of moles of CH_3CO_2H and $CH_3CO_2^-$ are both approximately equal to $\frac{0.00250 \text{ mol}}{2} = 0.00125 \text{ mol}$, and their concentrations are the same.

Since the amount of the added base is smaller than the original amount of the acid, the equivalence point has not been reached, the solution remains a buffer, and we can use the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_\text{a} + \log\frac{[\text{Base}]}{[\text{Acid}]} = -\log(K_\text{a}) + \log\frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = -\log(1.8\times10^{-5}) + \log(1)$$

(as the concentrations of CH_3CO_2^- and $\text{CH}_3\text{CO}_2\text{H}$ are the same)

Thus:

$$\text{pH} = -\log(1.8\times10^{-5}) = 4.74$$

(the pH = the pK_a at the halfway point in a titration of a weak acid)

(d) After 37.50 mL of NaOH is added, the amount of NaOH is 0.03750 L × 0.100 *M* = 0.003750 mol NaOH. Since this is past the equivalence point, the excess hydroxide ions will make the solution basic, and we can again use stoichiometric calculations to determine the pH:

$$[\text{OH}^-] = \frac{(0.003750\text{ mol} - 0.00250\text{ mol})}{0.06250\text{ L}} = 2.00\times10^{-2}\ M$$

So:

$$\text{pOH} = -\log(2.00\times10^{-2}) = 1.70,\ \text{and pH} = 14.00 - 1.70 = 12.30$$

Note that this result is the same as for the strong acid-strong base titration example provided, since the amount of the strong base added moves the solution past the equivalence point.

? Exercise 11.3.2

Calculate the pH for the weak acid/strong base titration between 50.0 mL of 0.100 *M* HCOOH(*aq*) (formic acid) and 0.200 *M* NaOH (titrant) at the listed volumes of added base:

a. 0.00 mL,
b. 15.0 mL,
c. 25.0 mL, and
d. 30.0 mL.

Answer a

0.00 mL: 2.37

Answer b

15.0 mL: 3.92

Answer c

25.00 mL: 8.29

Answer d

30.0 mL: 12.097

Acid-Base Indicators

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colorless substance in any aqueous solution with a hydronium ion concentration greater than 5.0 × 10^{-9} *M* (pH < 8.3). In more basic solutions where the hydronium ion concentration is less than 5.0 × 10^{-9} *M* (pH > 8.3), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called acid-base indicators. Acid-base indicators are either weak organic acids or weak organic bases.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use HIn as a simple representation for the complex methyl orange molecule:

$$\underbrace{\text{HIn(aq)}}_{\text{red}} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+\text{(aq)} + \underbrace{\text{In}^-\text{(aq)}}_{\text{yellow}}$$

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]} = 4.0 \times 10^{-4}$$

The anion of methyl orange, In^-, is yellow, and the nonionized form, HIn, is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Chatelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

An indicator's color is the visible result of the ratio of the concentrations of the two species In^- and HIn. If most of the indicator (typically about 60−90% or more) is present as In^-, then we see the color of the In^- ion, which would be yellow for methyl orange. If most is present as HIn, then we see the color of the HIn molecule: red for methyl orange. For methyl orange, we can rearrange the equation for K_a and write:

$$\frac{[In^-]}{[HIn]} = \frac{[\text{substance with yellow color}]}{[\text{substance with red color}]} = \frac{K_a}{[H_3O^+]} \tag{11.3.6}$$

Equation 11.3.6 shows us how the ratio of $\frac{[In^-]}{[HIn]}$ varies with the concentration of hydronium ion. The above expression describing the indicator equilibrium can be rearranged:

$$\frac{[H_3O^+]}{K_a} = \frac{[HIn]}{[In^-]} \tag{11.3.7}$$

$$\log\left(\frac{[H_3O^+]}{K_a}\right) = \log\left(\frac{[HIn]}{[In^-]}\right) \tag{11.3.8}$$

$$\log([H_3O^+]) - \log(K_a) = -\log\left(\frac{[In^-]}{[HIn]}\right) \tag{11.3.9}$$

$$-pH + pK_a = -\log\left(\frac{[In^-]}{[HIn]}\right) \tag{11.3.10}$$

$$pH = pK_a + \log\left(\frac{[In^-]}{[HIn]}\right) \tag{11.3.11}$$

or in general terms

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{11.3.12}$$

Equation 11.3.12 is the same as the *Henderson-Hasselbalch equation*, which can be used to describe the equilibrium of indicators.

When $[H_3O^+]$ has the same numerical value as K_a, the ratio of $[In^-]$ to [HIn] is equal to 1, meaning that 50% of the indicator is present in the red form (HIn) and 50% is in the yellow ionic form (In^-), and the solution appears orange in color. When the hydronium ion concentration increases to 8×10^{-4} *M* (a pH of 3.1), the solution turns red. No change in color is visible for any further increase in the hydronium ion concentration (decrease in pH). At a hydronium ion concentration of 4×10^{-5} *M* (a pH of 4.4), most of the indicator is in the yellow ionic form, and a further decrease in the hydronium ion concentration (increase in pH) does not produce a visible color change. The pH range between 3.1 (red) and 4.4 (yellow) is the color-change interval of methyl orange; the pronounced color change takes place between these pH values.

There are many different acid-base indicators that cover a wide range of pH values and can be used to determine the approximate pH of an unknown solution by a process of elimination. Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pHs. Figure 11.3.2 presents several indicators, their colors, and their color-change intervals.

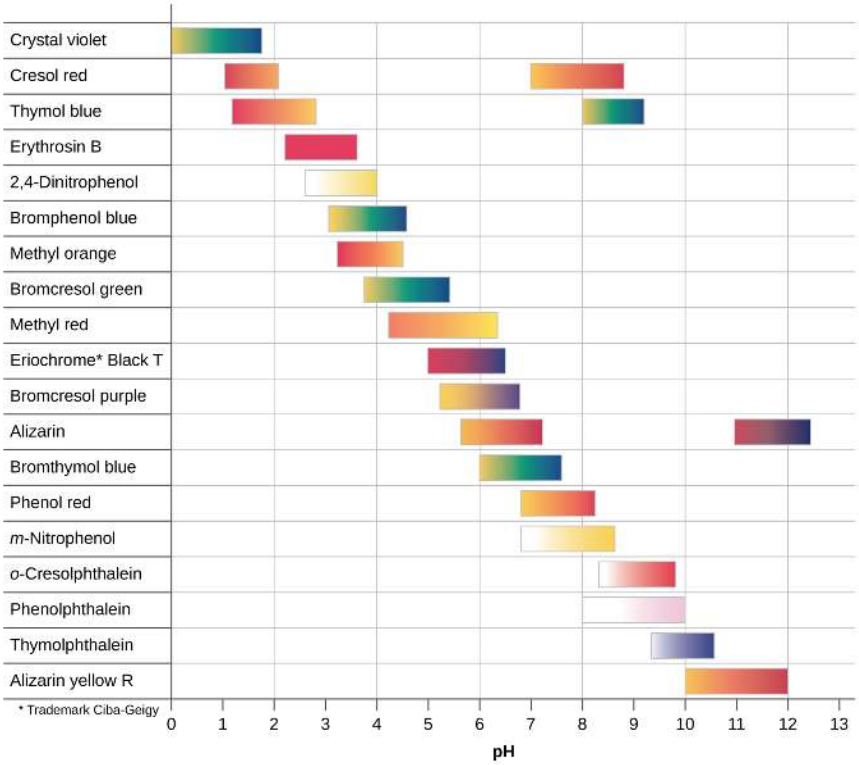


Figure 11.3.2: This chart illustrates the ranges of color change for several acid-base indicators.

Titration curves help us pick an indicator that will provide a sharp color change at the equivalence point. The best selection would be an indicator that has a color change interval that brackets the pH at the equivalence point of the titration.

The color change intervals of three indicators are shown in Figure 11.3.3 The equivalence points of both the titration of the strong acid and of the weak acid are located in the color-change interval of phenolphthalein. We can use it for titrations of either strong acid with strong base or weak acid with strong base.

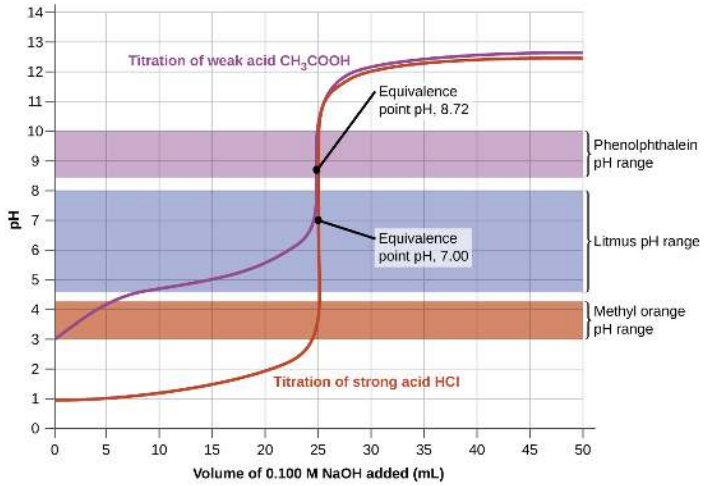


Figure 11.3.3: The graph shows a titration curve for the titration of 25.00 mL of 0.100 M CH_3CO_2H (weak acid) with 0.100 M NaOH (strong base) and the titration curve for the titration of HCl (strong acid) with NaOH (strong base). The pH ranges for the color change of phenolphthalein, litmus, and methyl orange are indicated by the shaded areas.

A graph is shown which is titled “Titration of Weak Acid.” The horizontal axis is labeled “Volume of 0.100 M N a O H added (m L)” and begins at 0 with markings every 5 units up to 50. The vertical axis is labeled “p H” and begins at 0 and increases by single units up to 14. A red curve is drawn on the graph. The curve begins at (0, 3) and passes through the points (5, 4.1), (10, 4.7), (15, 5), (20, 5.5), and (22.5, 6), after which it rapidly increases, forming a vertical section centered at the point (25, 8.7). The rapid increase of the curve then levels off and the curve passes through the points (30, 12), (35, 12.4), (40, 12.5), (45, 12.6), and (50, 12.6). A brown rectangle extends horizontally across the graph covering the p H of 3 to 4.2 range. To the right, this rectangle is labeled “Methyl orange p H range.” A blue rectangle extends horizontally across the graph covering the p H of 4.6 to 8 range. To the right, this rectangle is labeled “Litmus p H range.” A purple rectangle extends horizontally across the graph covering the p H of 8.4 to 10 range. To the right, this rectangle is labeled “Phenolphthalein p H range.” The midpoint of the vertical segment of the curve is labeled “Equivalence point p H, 8.72.”

Litmus is a suitable indicator for the HCl titration because its color change brackets the equivalence point. However, we should not use litmus for the CH_3CO_2H titration because the pH is within the color-change interval of litmus when only about 12 mL of NaOH has been added, and it does not leave the range until 25 mL has been added. The color change would be very gradual, taking place during the addition of 13 mL of NaOH, making litmus useless as an indicator of the equivalence point.

We could use methyl orange for the HCl titration, but it would not give very accurate results: (1) It completes its color change slightly before the equivalence point is reached (but very close to it, so this is not too serious); (2) it changes color, as Figure 11.3.2 demonstrates, during the addition of nearly 0.5 mL of NaOH, which is not so sharp a color change as that of litmus or phenolphthalein; and (3) it goes from yellow to orange to red, making detection of a precise endpoint much more challenging than the colorless to pink change of phenolphthalein. Figure 11.3.2 shows us that methyl orange would be completely useless as an indicator for the CH_3CO_2H titration. Its color change begins after about 1 mL of NaOH has been added and ends when about 8 mL has been added. The color change is completed long before the equivalence point (which occurs when 25.0 mL of NaOH has been added) is reached and hence provides no indication of the equivalence point.

We base our choice of indicator on a calculated pH, the pH at the equivalence point. At the equivalence point, equimolar amounts of acid and base have been mixed, and the calculation becomes that of the pH of a solution of the salt resulting from the titration.

Summary

A titration curve is a graph that relates the change in pH of an acidic or basic solution to the volume of added titrant. The characteristics of the titration curve are dependent on the specific solutions being titrated. The pH of the solution at the equivalence point may be greater than, equal to, or less than 7.00. The choice of an indicator for a given titration depends on the expected pH at the equivalence point of the titration, and the range of the color change of the indicator.

Glossary

acid-base indicator

organic acid or base whose color changes depending on the pH of the solution it is in

color-change interval

range in pH over which the color change of an indicator takes place

titration curve

plot of the pH of a solution of acid or base versus the volume of base or acid added during a titration

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11.4: Reaction Stoichiometry in Solutions- Oxidation-Reduction Titrations

Analytical titrations using redox reactions were introduced shortly after the development of acid–base titrimetry. The earliest **Redox titration** took advantage of the oxidizing power of chlorine. In 1787, Claude Berthollet introduced a method for the quantitative analysis of chlorine water (a mixture of Cl_2, HCl, and HOCl) based on its ability to oxidize indigo, a dye that is colorless in its oxidized state. In 1814, Joseph Gay-Lussac developed a similar method for determining chlorine in bleaching powder. In both methods the end point is a change in color. Before the equivalence point the solution is colorless due to the oxidation of indigo. After the equivalence point, however, unreacted indigo imparts a permanent color to the solution.

The number of redox titrimetric methods increased in the mid-1800s with the introduction of MnO_4^-, $Cr_2O_7^{2-}$, and I_2 as oxidizing titrants, and of Fe^{2+} and $S_2O_3^{2-}$ as reducing titrants. Even with the availability of these new titrants, redox titrimetry was slow to develop due to the lack of suitable indicators. A titrant can serve as its own indicator if its oxidized and reduced forms differ significantly in color. For example, the intensely purple MnO_4^- ion serves as its own indicator since its reduced form, Mn^{2+}, is almost colorless. Other titrants require a separate indicator. The first such indicator, diphenylamine, was introduced in the 1920s. Other redox indicators soon followed, increasing the applicability of redox titrimetry.

Redox Titration Curves

To evaluate a redox titration we need to know the shape of its titration curve. In an acid–base titration or a complexation titration, the titration curve shows how the concentration of H_3O^+ (as pH) or M^{n+} (as pM) changes as we add titrant. For a redox titration it is convenient to monitor the titration reaction's potential instead of the concentration of one species.

You may recall from Chapter 6 that the Nernst equation relates a solution's potential to the concentrations of reactants and products participating in the redox reaction. Consider, for example, a titration in which a titrand in a reduced state, A_{red}, reacts with a titrant in an oxidized state, B_{ox}.

$$A_{red} + B_{ox} \rightleftharpoons B_{red} + A_{ox} \tag{11.4.1}$$

where A_{ox} is the titrand's oxidized form, and B_{red} is the titrant's reduced form. The reaction's potential, E_{rxn}, is the difference between the reduction potentials for each half-reaction.

$$E_{rxn} = E_{B_{ox}/B_{red}} - E_{A_{ox}/A_{red}} \tag{11.4.2}$$

After each addition of titrant the reaction between the titrand and the titrant reaches a state of equilibrium. Because the potential at equilibrium is zero, the titrand's and the titrant's reduction potentials are identical.

$$E_{B_{ox}/B_{red}} = E_{A_{ox}/A_{red}} \tag{11.4.3}$$

This is an important observation because we can use either half-reaction to monitor the titration's progress.

Before the equivalence point the titration mixture consists of appreciable quantities of the titrand's oxidized and reduced forms. The concentration of unreacted titrant, however, is very small. The potential, therefore, is easier to calculate if we use the Nernst equation for the titrand's half-reaction

$$E_{rxn} = E^o_{A_{ox}/A_{red}} - \frac{RT}{nF}\ln\frac{[A_{red}]}{[A_{ox}]} \tag{11.4.4}$$

> Although the Nernst equation is written in terms of the half-reaction's standard state potential, a matrix-dependent **formal potential** often is used in its place. See Appendix 13 for the standard state potentials and formal potentials for selected half-reactions.

After the equivalence point it is easier to calculate the potential using the Nernst equation for the titrant's half-reaction.

$$E_{rxn} = E^o_{B_{ox}/B_{red}} - \frac{RT}{nF}\ln\frac{[B_{red}]}{[B_{ox}]} \tag{11.4.5}$$

Calculating the Titration Curve

Let's calculate the titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in a matrix of 1 M $HClO_4$. The reaction in this case is

$$Fe^{2+}(aq) + Ce^{4+}(aq) \rightleftharpoons Ce^{3+}(aq) + Fe^{3+}(aq) \tag{9.15}$$

In 1 M $HClO_4$, the formal potential for the reduction of Fe^{3+} to Fe^{2+} is +0.767 V, and the formal potential for the reduction of Ce^{4+} to Ce^{3+} is +1.70 V.

Because the equilibrium constant for reaction 9.15 is very large—it is approximately 6×10^{15}—we may assume that the analyte and titrant react completely.

Step 1

Calculate the volume of titrant needed to reach the equivalence point.

The first task is to calculate the volume of Ce^{4+} needed to reach the titration's equivalence point. From the reaction's stoichiometry we know that

$$\text{moles } Fe^{2+} = \text{moles } Ce^{4+} \tag{11.4.6}$$

$$M_{Fe} \times V_{Fe} = M_{Ce} \times V_{Ce} \tag{11.4.7}$$

Solving for the volume of Ce^{4+} gives the equivalence point volume as

$$V_{eq} = V_{Ce} = \frac{M_{Fe}V_{Fe}}{M_{Ce}} = \frac{(0.100\text{ M})(50.0\text{ mL})}{(0.100\text{ M})} = 50.0\text{ mL} \tag{11.4.8}$$

Step 2:

alculate the potential before the equivalence point by determining the concentrations of the titrand's oxidized and reduced forms, and using the Nernst equation for the titrand's reduction half-reaction.

Before the equivalence point, the concentration of unreacted Fe^{2+} and the concentration of Fe^{3+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Fe^{3+}/Fe^{2+} half-reaction.

$$E = E^o_{Fe^{3+}/Fe^{2+}} - \frac{RT}{nF}\log\frac{[Fe^{2+}]}{[Fe^{3+}]} = +0.767\text{V} - 0.05916\log\frac{[Fe^{2+}]}{[Fe^{3+}]} \tag{9.16}$$

For example, the concentrations of Fe^{2+} and Fe^{3+} after adding 10.0 mL of titrant are

$$[Fe^{2+}] = \frac{\text{initial moles } Fe^{2+} - \text{moles } Ce^{4+} \text{ added}}{\text{total volume}} = \frac{M_{Fe}V_{Fe} - M_{Ce}V_{Ce}}{V_{Fe} + V_{Ce}} \tag{11.4.9}$$

$$= \frac{(0.100\text{ M})(50.0\text{ mL}) - (0.100\text{ M})(10.0\text{ mL})}{50.0\text{ mL} + 10.0\text{ mL}} = 6.67 \times 10^{-2}\text{ M} \tag{11.4.10}$$

$$[Fe^{3+}] = \frac{\text{moles } Ce^{4+} \text{ added}}{\text{total volume}} = \frac{M_{Ce}V_{Ce}}{V_{Fe} + V_{Ce}} \tag{11.4.11}$$

$$= \frac{(0.100\text{ M})(10.0\text{ mL})}{50.0\text{ mL} + 10.0\text{ mL}} = 1.67 \times 10^{-2}\text{ M} \tag{11.4.12}$$

Substituting these concentrations into equation 9.16 gives a potential of

$$E = +0.767\text{ V} - 0.05916\log\frac{6.67 \times 10^{-2}\text{ M}}{1.67 \times 10^{-2}\text{ M}} = +0.731\text{ V} \tag{11.4.13}$$

Step 3:

Calculate the potential after the equivalence point by determining the concentrations of the titrant's oxidized and reduced forms, and using the Nernst equation for the titrant's reduction half-reaction.

After the equivalence point, the concentration of Ce^{3+} and the concentration of excess Ce^{4+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Ce^{4+}/Ce^{3+} half-reaction.

$$E = E^o_{Ce^{4+}/Ce^{3+}} - \frac{RT}{nF}\log\frac{[Ce^{3+}]}{[Ce^{4+}]} = +1.70\text{ V} - 0.05916\log\frac{[Ce^{3+}]}{[Ce^{4+}]} \tag{9.17}$$

For example, after adding 60.0 mL of titrant, the concentrations of Ce^{3+} and Ce^{4+} are

$$[Ce^{3+}] = \frac{\text{initial moles } Fe^{2+}}{\text{total volume}} = \frac{M_{Fe}V_{Fe}}{V_{Fe}+V_{Ce}} \tag{11.4.14}$$

$$= \frac{(0.100\text{ M})(50.0\text{ mL})}{50.0\text{ mL}+60.0\text{ mL}} = 4.55\times10^{-3}\text{ M} \tag{11.4.15}$$

$$[Ce^{4+}] = \frac{\text{moles } Ce^{4+}\text{ added} - \text{initial moles } Fe^{2+}}{\text{total volume}} = \frac{M_{Ce}V_{Ce}-M_{Fe}V_{Fe}}{V_{Fe}+V_{Ce}} \tag{11.4.16}$$

$$= \frac{(0.100\text{ M})(60.0\text{ mL})-(0.100\text{ M})(50.0\text{ mL})}{50.0\text{ mL}+60.0\text{ mL}} = 9.09\times10^{-3}\text{ M} \tag{11.4.17}$$

Substituting these concentrations into Equation 9.17 gives a potential of

$$E = +1.70\text{ V} - 0.05916\log\frac{4.55\times10^{-2}\text{ M}}{9.09\times10^{-3}\text{ M}} = +1.66\text{ V} \tag{11.4.18}$$

Step 4

Calculate the potential at the equivalence point.

At the titration's equivalence point, the potential, E_{eq}, in equation 9.16 and equation 9.17 are identical. Adding the equations together to gives

$$2E_{eq} = E^o_{Fe^{3+}/Fe^{2+}} + E^o_{Ce^{4+}/Ce^{3+}} - 0.05916\log\frac{[Fe^{2+}][Ce^{3+}]}{[Fe^{3+}][Ce^{4+}]} \tag{11.4.19}$$

Because $[Fe^{2+}] = [Ce^{4+}]$ and $[Ce^{3+}] = [Fe^{3+}]$ at the equivalence point, the log term has a value of zero and the equivalence point's potential is

$$E_{eq} = \frac{E^o_{Fe^{3+}/Fe^{2+}} + E^o_{Ce^{4+}/Ce^{3+}}}{2} = \frac{0.767\text{ V}+1.70\text{ V}}{2} = 1.23\text{ V} \tag{11.4.20}$$

Additional results for this titration curve are shown in Table 9.15 and Figure 9.36.

Table 9.15: *Data for the Titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}*

Volume of Ce^{4+} (mL)	*E* (V)	Volume Ce^{4+} (mL)	*E* (V)
10.0	0.731	60.0	1.66
20.0	0.757	70.0	1.68
30.0	0.777	80.0	1.69
40.0	0.803	90.0	1.69
50.0	1.23	100.0	1.70

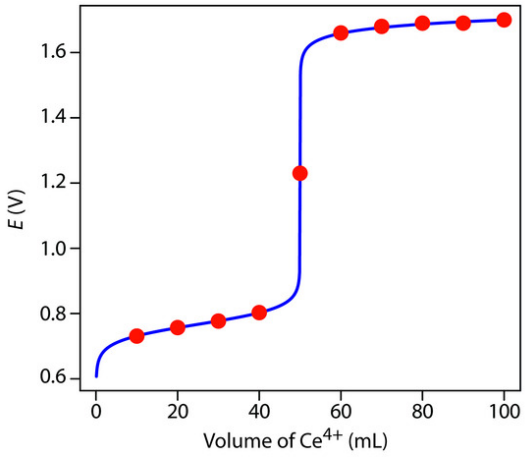


Figure 9.36 *Titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}. The red points correspond to the data in Table 9.15. The blue line shows the complete titration curve.*

Exercise 11.4.1

Calculate the titration curve for the titration of 50.0 mL of 0.0500 M Sn^{2+} with 0.100 M Tl^{3+}. Both the titrand and the titrant are 1.0 M in HCl. The titration reaction is

$$Sn^{2+}(aq) + Tl^{3+}(aq) \rightarrow Sn^{4+}(aq) + Tl^{+}(aq) \tag{11.4.21}$$

Click here to review your answer to this exercise.

Sketching a Redox Titration Curve

To evaluate the relationship between a titration's equivalence point and its end point we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching a redox titration curve. Our goal is to sketch the titration curve quickly, using as few calculations as possible. Let's use the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in a matrix of 1 M $HClO_4$.

This is the same example that we used in developing the calculations for a redox titration curve. You can review the results of that calculation in Table 9.15 and Figure 9.36.

We begin by calculating the titration's equivalence point volume, which, as we determined earlier, is 50.0 mL. Next, we draw our axes, placing the potential, *E*, on the *y*-axis and the titrant's volume on the *x*-axis. To indicate the equivalence point's volume, we draw a vertical line corresponding to 50.0 mL of Ce^{4+}. Figure 9.37a shows the result of the first step in our sketch.

Before the equivalence point, the potential is determined by a redox buffer of Fe^{2+} and Fe^{3+}. Although we can easily calculate the potential using the Nernst equation, we can avoid this calculation by making a simple assumption. You may recall from Chapter 6 that a redox buffer operates over a range of potentials that extends approximately ±(0.05916/*n*) unit on either side of $E^{o}_{Fe^{3+}/Fe^{2+}}$. The potential is at the buffer's lower limit

$$\mathrm{E} = E^{o}_{Fe^{3+}/Fe^{2+}} - 0.05916 \tag{11.4.22}$$

when the concentration of Fe^{2+} is 10× greater than that of Fe^{3+}. The buffer reaches its upper potential

$$\mathrm{E} = E^{o}_{Fe^{3+}/Fe^{2+}} + 0.05916 \tag{11.4.23}$$

when the concentration of Fe^{2+} is 10× smaller than that of Fe^{3+}. The redox buffer spans a range of volumes from approximately 10% of the equivalence point volume to approximately 90% of the equivalence point volume.

Figure 9.37b shows the second step in our sketch. First, we superimpose a ladder diagram for Fe^{2+} on the *y*-axis, using its $E^{o}_{Fe^{3+}/Fe^{2+}}$ value of 0.767 V and including the buffer's range of potentials. Next, we add points representing the pH at 10% of the equivalence point volume (a potential of 0.708 V at 5.0 mL) and at 90% of the equivalence point volume (a potential of 0.826 V at 45.0 mL).

> *We used a similar approach when sketching the acid–base titration curve for the titration of acetic acid with NaOH.*

The third step in sketching our titration curve is to add two points after the equivalence point. Here the potential is controlled by a redox buffer of Ce^{3+} and Ce^{4+}. The redox buffer is at its lower limit of $E = E^{o}_{Ce^{4+}/Ce^{3+}} - 0.05916$ when the titrant reaches 110% of the equivalence point volume and the potential is $E^{o}_{Ce^{4+}/Ce^{3+}}$ when the volume of Ce^{4+} is $2 \times V_{eq}$.

Figure 9.37c shows the third step in our sketch. First, we add a ladder diagram for Ce^{4+}, including its buffer range, using its $E^{o}_{Ce^{4+}/Ce^{3+}}$ value of 1.70 V. Next, we add points representing the potential at 110% of V_{eq} (a value of 1.66 V at 55.0 mL) and at 200% of V_{eq} (a value of 1.70 V at 100.0 mL).

> *We used a similar approach when sketching the complexation titration curve for the titration of Mg^{2+} with EDTA.*

Next, we draw a straight line through each pair of points, extending the line through the vertical line representing the equivalence point's volume (Figure 9.37d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure 9.37e). A comparison of our sketch to the exact titration curve (Figure 9.37f) shows that they are in close agreement.

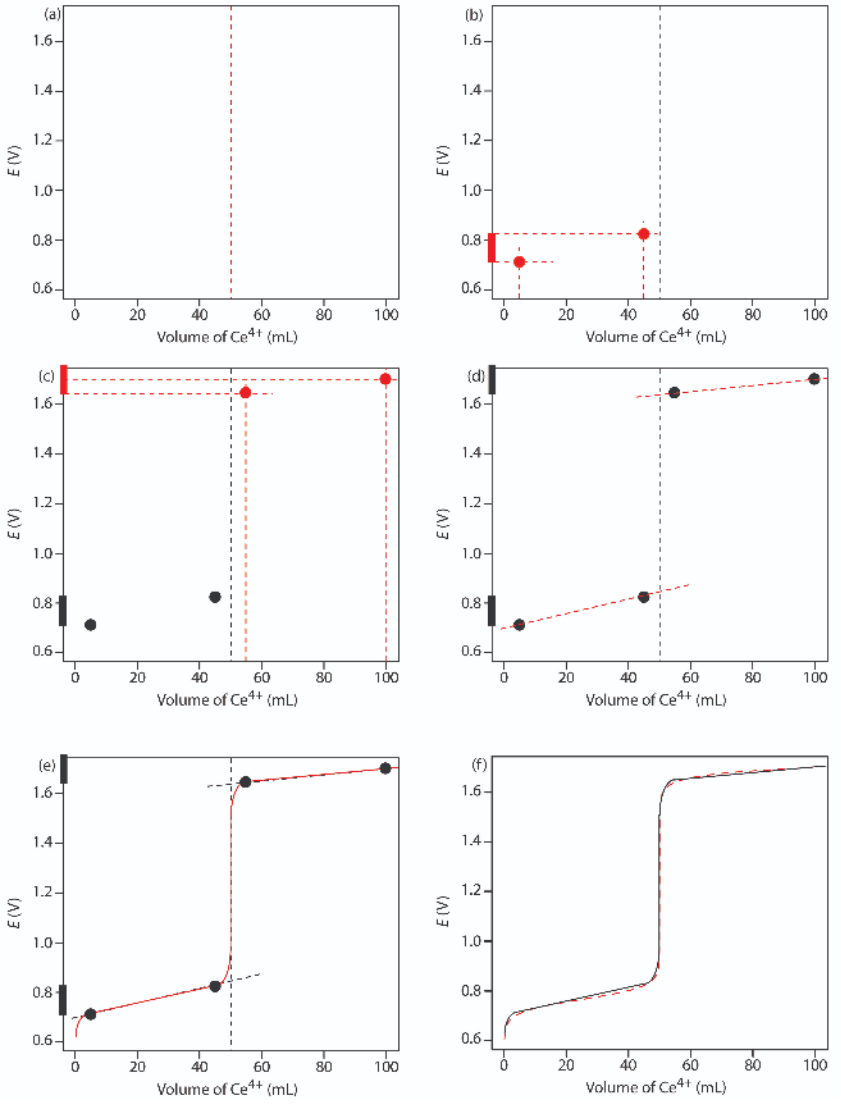


Figure 9.37: *Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in 1 M $HClO_4$: (a) locating the equivalence point volume; (b) plotting two points before the equivalence*

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point; (c) plotting two points after the equivalence point; (d) preliminary approximation of titration curve using straight-lines; (e) final approximation of titration curve using a smooth curve; (f) comparison of approximate titration curve (solid black line) and exact titration curve (dashed red line). See the text for additional details.

Exercise 11.4.2

Sketch the titration curve for the titration of 50.0 mL of 0.0500 M Sn^{4+} with 0.100 M Tl^{+}. Both the titrand and the titrant are 1.0 M in HCl. The titration reaction is

$$Sn^{2+}(aq) + Tl^{3+}(aq) \rightarrow Sn^{4+}(aq) + Tl^{+}(aq) \tag{11.4.24}$$

Compare your sketch to your calculated titration curve from Practice Exercise 9.17.

Click here to review your answer to this exercise.

9.4.2 Selecting and Evaluating the End point

A redox titration's equivalence point occurs when we react stoichiometrically equivalent amounts of titrand and titrant. As is the case with acid–base and complexation titrations, we estimate the equivalence point of a complexation titration using an experimental end point. A variety of methods are available for locating the end point, including indicators and sensors that respond to a change in the solution conditions.

Where is the Equivalence Point?

For an acid–base titration or a complexometric titration the equivalence point is almost identical to the inflection point on the steeping rising part of the titration curve. If you look back at Figure 9.7 and Figure 9.28, you will see that the inflection point is in the middle of this steep rise in the titration curve, which makes it relatively easy to find the equivalence point when you sketch these titration curves. We call this a **symmetric equivalence point**. If the stoichiometry of a redox titration is symmetric—one mole of titrant reacts with each mole of titrand—then the equivalence point is symmetric. If the titration reaction's stoichiometry is not 1:1, then the equivalence point is closer to the top or to bottom of the titration curve's sharp rise. In this case we have an **asymmetric equivalence point**.

Example 11.4.1

Derive a general equation for the equivalence point's potential when titrating Fe^{2+} with MnO_4^-.

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O \tag{11.4.25}$$

(We often use H^+ instead of H_3O^+ when writing a redox reaction.)

Solution

The half-reactions for Fe^{2+} and MnO_4^- are

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^- \tag{11.4.26}$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \tag{11.4.27}$$

for which the Nernst equations are

$$E = E^o_{Fe^{3+}/Fe^{2+}} - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \tag{11.4.28}$$

$$E = E^o_{MnO_4^-/Mn^{2+}} - \frac{0.05916}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8} \tag{11.4.29}$$

Before adding these two equations together we must multiply the second equation by 5 so that we can combine the log terms; thus

$$6E = E^o_{Fe^{3+}/Fe^{2+}} + 5E^o_{MnO_4^-/Mn^{2+}} - 0.05916 \log \frac{[Fe^{2+}][Mn^{2+}]}{[Fe^{3+}][MnO_4^-][H^+]^8} \tag{11.4.30}$$

At the equivalence point we know that

$$[Fe^{2+}] = 5 \times [MnO_4^-] \tag{11.4.31}$$

$$[Fe^{3+}] = 5 \times [Mn^{2+}] \tag{11.4.32}$$

Substituting these equalities into the previous equation and rearranging gives us a general equation for the potential at the equivalence point.

$$6E_{eq} = E^o_{Fe^{3+}/Fe^{2+}} + 5E^o_{MnO_4^-/Mn^{2+}} - 0.05916 \log \frac{5[MnO_4^-][Mn^{2+}]}{5[Mn^{2+}][MnO_4^-][H^+]^8} \tag{11.4.33}$$

$$E_{eq} = \frac{E^o_{Fe^{3+}/Fe^{2+}} + 5E^o_{MnO_4^-/Mn^{2+}}}{6} - \frac{0.05916}{6} \log \frac{1}{[H^+]^8} \tag{11.4.34}$$

$$E_{eq} = \frac{E^o_{Fe^{3+}/Fe^{2+}} + 5E^o_{MnO_4^-/Mn^{2+}}}{6} + \frac{0.05916 \times 8}{6} \log [H^+] \tag{11.4.35}$$

$$E_{eq} = \frac{E^o_{Fe^{3+}/Fe^{2+}} + 5E^o_{MnO_4^-/Mn^{2+}}}{6} - 0.07888 pH \tag{11.4.36}$$

Our equation for the equivalence point has two terms. The first term is a weighted average of the titrand's and the titrant's standard state potentials, in which the weighting factors are the number of electrons in their respective half-reactions. (Instead of standard state potentials, you can use formal potentials.) The second term shows that E_{eq} for this titration is pH-dependent. At a pH of 1 (in H_2SO_4), for example, the equivalence point has a potential of

$$E_{eq} = \frac{0.768 + 5 \times 1.51}{6} - 0.07888 \times 1 = 1.31 \text{ V} \tag{11.4.37}$$

Figure 9.38 shows a typical titration curve for titration of Fe^{2+} with MnO_4^-. Note that the titration's equivalence point is asymmetrical.

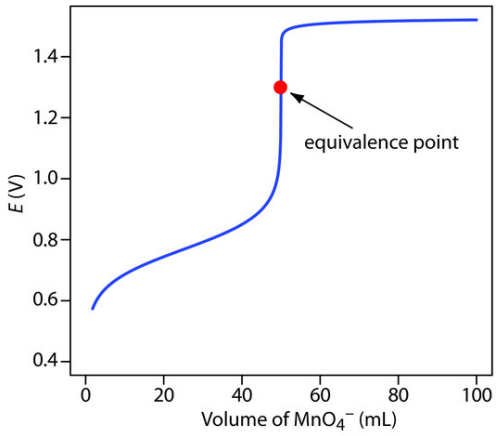


Figure 9.38: *Titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.0200 M MnO_4^- at a fixed pH of 1 (using H_2SO_4). The equivalence point is shown by the red dot.*

Exercise 11.4.3

Derive a general equation for the equivalence point's potential for the titration of U^{4+} with Ce^{4+}. The unbalanced reaction is

$$Ce^{4+}(aq) + U^{4+}(aq) \rightarrow UO_2^{2+}(aq) + Ce^{3+}(aq) \tag{11.4.38}$$

What is the equivalence point's potential if the pH is 1?

Click here to review your answer to this exercise.

Finding the End point with an Indicator

Three types of indicators are used to signal a redox titration's end point. The oxidized and reduced forms of some titrants, such as MnO_4^-, have different colors. A solution of MnO_4^- is intensely purple. In an acidic solution, however, permanganate's reduced form, Mn^{2+}, is nearly colorless. When using MnO_4^- as a titrant, the titrand's solution remains colorless until the equivalence point. The first drop of excess MnO_4^- produces a permanent tinge of purple, signaling the end point.

Some indicators form a colored compound with a specific oxidized or reduced form of the titrant or the titrand. Starch, for example, forms a dark blue complex with I_3^-. We can use this distinct color to signal the presence of excess I_3^- as a titrant—a change in color from colorless to blue—or the completion of a reaction consuming I_3^- as the titrand—a change in color from blue to colorless. Another example of a specific indicator is thiocyanate, SCN^-, which forms a soluble red-colored complex of $Fe(SCN)^{2+}$ with Fe^{3+}.

The most important class of indicators are substances that do not participate in the redox titration, but whose oxidized and reduced forms differ in color. When we add a **redox indicator** to the titrand, the indicator imparts a color that depends on the solution's potential. As the solution's potential changes with the addition of titrant, the indicator changes oxidation state and changes color, signaling the end point.

To understand the relationship between potential and an indicator's color, consider its reduction half-reaction

$$\mathrm{In_{ox}} + ne^- \rightleftharpoons \mathrm{In_{red}} \tag{11.4.39}$$

where In_{ox} and In_{red} are, respectively, the indicator's oxidized and reduced forms.

> *For simplicity, In_{ox} and In_{red} are shown without specific charges. Because there is a change in oxidation state, In_{ox} and In_{red} cannot both be neutral.*

The Nernst equation for this half-reaction is

$$E = E^o_{\mathrm{In_{ox}/In_{red}}} - \frac{0.05916}{n} \log \frac{[\mathrm{In_{red}}]}{[\mathrm{In_{ox}}]} \tag{11.4.40}$$

As shown in Figure 9.39, if we assume that the indicator's color changes from that of In_{ox} to that of In_{red} when the ratio $[In_{red}]/[In_{ox}]$ changes from 0.1 to 10, then the end point occurs when the solution's potential is within the range

$$E = E^o_{\mathrm{In_{ox}/In_{red}}} \pm \frac{0.05916}{n} \tag{11.4.41}$$

> *This is the same approach we took in considering acid–base indicators and complexation indicators.*

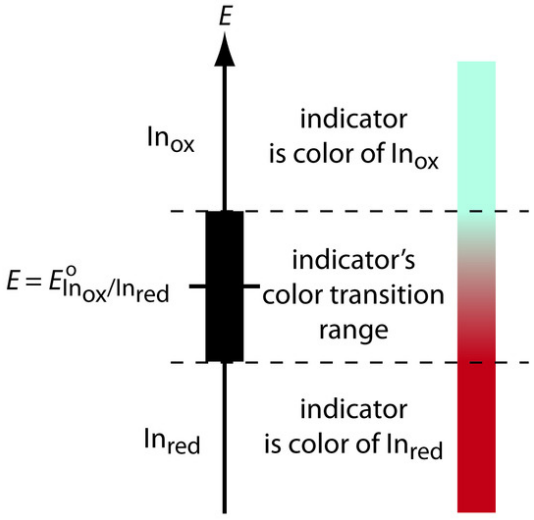


Figure 9.39 Diagram showing the relationship between E and an indicator's color. The ladder diagram defines potentials where In_{red} and In_{ox} are the predominate species. The indicator changes color when E is within the range

$$E = E^{o}_{Inox/Inred} \pm 0.05916/n$$

A partial list of redox indicators is shown in Table 9.16. Examples of appropriate and inappropriate indicators for the titration of Fe^{2+} with Ce^{4+} are shown in Figure 9.40.

Table 9.16 Selected Examples of Redox Indicators

Indicator	Color of In_{ox}	Color of In_{red}	$E^{o}In_{ox}/In_{red}$
indigo tetrasulfate	blue	colorless	0.36
methylene blue	blue	colorless	0.53
diphenylamine	violet	colorless	0.75
diphenylamine sulfonic acid	red-violet	colorless	0.85
tris(2,2´-bipyridine)iron	pale blue	red	1.120
ferroin	pale blue	red	1.147
tris(5-nitro-1,10-phenanthroline)iron	pale blue	red-violet	1.25

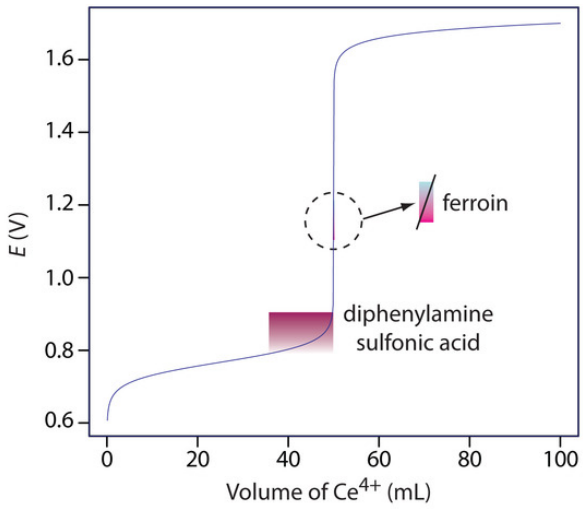


Figure 9.40: *Titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}. The end point transitions for the indicators diphenylamine sulfonic acid and ferroin are superimposed on the titration curve. Because the transition for ferroin is too small to see on the scale of the x-axis—it requires only 1–2 drops of titrant—the color change is expanded to the right.*

Other Methods for Finding the End point

Another method for locating a redox titration's end point is a potentiometric titration in which we monitor the change in potential while adding the titrant to the titrand. The end point is found by visually examining the titration curve. The simplest experimental design for a potentiometric titration consists of a Pt indicator electrode whose potential is governed by the titrand's or titrant's redox half-reaction, and a reference electrode that has a fixed potential. A further discussion of potentiometry is found in Chapter 11. Other methods for locating the titration's end point include thermometric titrations and spectrophotometric titrations.

The best way to appreciate the theoretical and practical details discussed in this section is to carefully examine a typical redox titrimetric method. Although each method is unique, the following description of the determination of the total chlorine residual in water provides an instructive example of a typical procedure. The description here is based on Method 4500-Cl B as published in *Standard Methods for the Examination of Water and Wastewater*, 20th Ed., American Public Health Association: Washington, D. C., 1998.

Representative Method 9.3: **Determination of Total Chlorine Residual**

Description of the Method

The chlorination of public water supplies produces several chlorine-containing species, the combined concentration of which is called the total chlorine residual. Chlorine may be present in a variety of states, including the free residual chlorine, consisting of Cl_2, HOCl and OCl^-, and the combined chlorine residual, consisting of NH_2Cl, $NHCl_2$, and NCl_3. The total chlorine residual is determined by using the oxidizing power of chlorine to convert I^- to I_3^-. The amount of I_3^- formed is then determined by titrating with $Na_2S_2O_3$ using starch as an indicator. Regardless of its form, the total chlorine residual is reported as if Cl_2 is the only source of chlorine, and is reported as mg Cl/L.

Procedure

Select a volume of sample requiring less than 20 mL of $Na_2S_2O_3$ to reach the end point. Using glacial acetic acid, acidify the sample to a pH of 3–4, and add about 1 gram of KI. Titrate with $Na_2S_2O_3$ until the yellow color of I_3^- begins to disappear. Add 1 mL of a starch indicator solution and continue titrating until the blue color of the starch–I_3^- complex disappears (Figure 9.41). Use a blank titration to correct the volume of titrant needed to reach the end point for reagent impurities.

Questions

1. Is this an example of a direct or an indirect analysis?

This is an indirect analysis because the chlorine-containing species do not react with the titrant. Instead, the total chlorine residual oxidizes I^- to I_3^-, and the amount of I_3^- is determined by titrating with $Na_2S_2O_3$.

2. Why does the procedure rely on an indirect analysis instead of directly titrating the chlorine-containing species using KI as a titrant?

Because the total chlorine residual consists of six different species, a titration with I^- does not have a single, well-defined equivalence point. By converting the chlorine residual to an equivalent amount of I_3^-, the indirect titration with $Na_2S_2O_3$ has a single, useful equivalence point.

Even if the total chlorine residual is from a single species, such as HOCl, a direct titration with KI is impractical. Because the product of the titration, I_3^-, imparts a yellow color, the titrand's color would change with each addition of titrant, making it difficult to find a suitable indicator.

3. Both oxidizing and reducing agents can interfere with this analysis. Explain the effect of each type of interferent has on the total chlorine residual.

An interferent that is an oxidizing agent converts additional I^- to I_3^-. Because this extra I_3^- requires an additional volume of $Na_2S_2O_3$ to reach the end point, we overestimate the total chlorine residual. If the interferent is a reducing agent, it reduces back to I^- some of the I_3^- produced by the reaction between the total chlorine residual and iodide. As a result. we underestimate the total chlorine residual.



Figure 9.41 Endpoint for the determination of the total chlorine residual. (a) Acidifying the sample and adding KI forms a brown solution of I_3^-. (b) Titrating with $Na_2S_2O_3$ converts I_3^- to I^- with the solution fading to a pale yellow color as we approach the end

point. (c) Adding starch forms the deep purple starch–I_3^- complex. (d) As the titration continues, the end point is a sharp transition from a purple to a colorless solution. The change in color from (c) to (d) typically takes 1–2 drops of titrant.

9.4.3 Quantitative Applications

Although many quantitative applications of redox titrimetry have been replaced by other analytical methods, a few important applications continue to be relevant. In this section we review the general application of redox titrimetry with an emphasis on environmental, pharmaceutical, and industrial applications. We begin, however, with a brief discussion of selecting and characterizing redox titrants, and methods for controlling the titrand's oxidation state.

Adjusting the Titrand's Oxidation State

If a redox titration is to be used in a quantitative analysis, the titrand must initially be present in a single oxidation state. For example, iron can be determined by a redox titration in which Ce^{4+} oxidizes Fe^{2+} to Fe^{3+}. Depending on the sample and the method of sample preparation, iron may initially be present in both the +2 and +3 oxidation states. Before titrating, we must reduce any Fe^{3+} to Fe^{2+}. This type of pretreatment can be accomplished using an auxiliary reducing agent or oxidizing agent.

A metal that is easy to oxidize—such as Zn, Al, and Ag—can serve as an **auxiliary reducing agent**. The metal, as a coiled wire or powder, is added to the sample where it reduces the titrand. Because any unreacted auxiliary reducing agent will react with the titrant, it must be removed before beginning the titration. This can be accomplished by simply removing the coiled wire, or by filtering.

An alternative method for using an auxiliary reducing agent is to immobilize it in a column. To prepare a reduction column an aqueous slurry of the finally divided metal is packed in a glass tube equipped with a porous plug at the bottom. The sample is placed at the top of the column and moves through the column under the influence of gravity or vacuum suction. The length of the reduction column and the flow rate are selected to ensure the analyte's complete reduction.

Two common reduction columns are used. In the **Jones reductor** the column is filled with amalgamated zinc, Zn(Hg), prepared by briefly placing Zn granules in a solution of $HgCl_2$. Oxidation of zinc

$$\mathrm{Zn(Hg)}(s) \rightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Hg}(l) + 2e^- \tag{11.4.42}$$

provides the electrons for reducing the titrand. In the **Walden reductor** the column is filled with granular Ag metal. The solution containing the titrand is acidified with HCl and passed through the column where the oxidation of silver

$$\mathrm{Ag}(s) + \mathrm{Cl}^-(aq) \rightarrow \mathrm{AgCl}(s) + e^- \tag{11.4.43}$$

provides the necessary electrons for reducing the titrand. Table 9.17 provides a summary of several applications of reduction columns.

Table 9.17 Examples of Reactions For Reducing a Titrand's Oxidation State Using a Reduction Column

Oxidized Titrand	Walden Reductor	Jones Reductor
Cr^{3+}	—	$Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$
Cu^{2+}	$Cu^{2+}(aq) + e^- \rightarrow Cu^{+}(aq)$	$Cu^{2+}(aq) + 2e^- \rightarrow Cr(s)$
Fe^{3+}	$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$
TiO^{2+}	—	$TiO^{2+}(aq) + 2H^+(aq) + e^- \rightarrow Ti^{3+}(aq) + H_2O(l)$
MoO_2^{2+}	$MoO_2^{2+}(aq) + e^- \rightarrow MoO_2^{+}(aq)$	$MoO_2^{2+}(aq) + 4H^+(aq) + 3e^- \rightarrow Mo^{3+}(aq) + 2H_2O(l)$
VO_2^{+}	$VO_2^{+}(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l)$	$VO_2^{+}(aq) + 4H^+(aq) + 3e^- \rightarrow V^{2+}(aq) + 2H_2O(l)$

Several reagents are commonly used as **auxiliary oxidizing agents**, including ammonium peroxydisulfate, $(NH_4)_2S_2O_8$, and hydrogen peroxide, H_2O_2. Peroxydisulfate is a powerful oxidizing agent

$$\mathrm{S_2O_8^{2-}}(aq) + 2e^- \rightarrow 2\mathrm{SO_4^{2-}}(aq) \tag{11.4.44}$$

capable of oxidizing Mn^{2+} to MnO_4^-, Cr^{3+} to $Cr_2O_7^{2-}$, and Ce^{3+} to Ce^{4+}. Excess peroxydisulfate is easily destroyed by briefly boiling the solution. The reduction of hydrogen peroxide in acidic solution

$$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l) \tag{11.4.45}$$

provides another method for oxidizing a titrand. Excess H_2O_2 is destroyed by briefly boiling the solution.

Selecting and Standardizing a Titrant

If it is to be used quantitatively, the titrant's concentration must remain stable during the analysis. Because a titrant in a reduced state is susceptible to air oxidation, most redox titrations use an oxidizing agent as the titrant. There are several common oxidizing titrants, including MnO_4^-, Ce^{4+}, $Cr_2O_7^{2-}$, and I_3^-. Which titrant is used often depends on how easy it is to oxidize the titrand. A titrand that is a weak reducing agent needs a strong oxidizing titrant if the titration reaction is to have a suitable end point.

The two strongest oxidizing titrants are MnO_4^- and Ce^{4+}, for which the reduction half-reactions are

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \tag{11.4.46}$$

$$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq) \tag{11.4.47}$$

Solutions of Ce4+ usually are prepared from the primary standard cerium ammonium nitrate, Ce(NO3)4•2NH4NO3, in 1 M H2SO4. When prepared using a reagent grade material, such as Ce(OH)4, the solution is standardized against a primary standard reducing agent such as Na2C2O4 or Fe2+ (prepared using iron wire) using ferroin as an indicator. Despite its availability as a primary standard and its ease of preparation, Ce4+ is not as frequently used as MnO4– because it is more expensive.

Note

The standardization reactions are

$$Ce^{4+}(aq) + Fe^{2+}(aq) \rightarrow Ce^{3+}(aq) + Fe^{3+}(aq) \tag{11.4.48}$$

$$2Ce^{4+}(aq) + H_2C_2O_4(aq) \rightarrow 2Ce^{3+}(aq) + 2CO_2(g) + 2H^+(aq) \tag{11.4.49}$$

Solutions of MnO_4^- are prepared from $KMnO_4$, which is not available as a primary standard. Aqueous solutions of permanganate are thermodynamically unstable due to its ability to oxidize water.

$$4\,MnO_4^-(aq) + 2H_2O(l) \rightleftharpoons 4MnO_2(s) + 3O_2(g) + 4OH^-(aq) \tag{11.4.50}$$

This reaction is catalyzed by the presence of MnO_2, Mn^{2+}, heat, light, and the presence of acids and bases. A moderately stable solution of permanganate can be prepared by boiling it for an hour and filtering through a sintered glass filter to remove any solid MnO_2 that precipitates. Standardization is accomplished against a primary standard reducing agent such as $Na_2C_2O_4$ or Fe^{2+} (prepared using iron wire), with the pink color of excess MnO_4^- signaling the end point. A solution of MnO_4^- prepared in this fashion is stable for 1–2 weeks, although the standardization should be rechecked periodically.

Note

The standardization reactions are

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l) \tag{11.4.51}$$

$$2\,MnO_4^-(aq) + 5H_2C_2O_4(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l) \tag{11.4.52}$$

Potassium dichromate is a relatively strong oxidizing agent whose principal advantages are its availability as a primary standard and the long term stability of its solutions. It is not, however, as strong an oxidizing agent as MnO_4^- or Ce^{4+}, which makes it less useful when the titrand is a weak reducing agent. Its reduction half-reaction is

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l) \tag{11.4.53}$$

Although a solution of $Cr_2O_7^{2-}$ is orange and a solution of Cr^{3+} is green, neither color is intense enough to serve as a useful indicator. Diphenylamine sulfonic acid, whose oxidized form is red-violet and reduced form is colorless, gives a very distinct end point signal with $Cr_2O_7^{2-}$.

Iodine is another important oxidizing titrant. Because it is a weaker oxidizing agent than MnO_4^-, Ce^{4+}, and $Cr_2O_7^{2-}$, it is useful only when the titrand is a stronger reducing agent. This apparent limitation, however, makes I_2 a more selective titrant for the

analysis of a strong reducing agent in the presence of a weaker reducing agent. The reduction half-reaction for I_2 is

$$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq) \tag{11.4.54}$$

Because iodine is not very soluble in water, solutions are prepared by adding an excess of I^-. The complexation reaction

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \tag{11.4.55}$$

increases the solubility of I_2 by forming the more soluble triiodide ion, I_3^-. Even though iodine is present as I_3^- instead of I_2, the number of electrons in the reduction half-reaction is unaffected.

$$I_3^-(aq) + 2e^- \rightleftharpoons 3I^-(aq) \tag{11.4.56}$$

Solutions of I_3^- are normally standardized against $Na_2S_2O_3$ using starch as a specific indicator for I_3^-.

Note

The standardization reaction is

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightarrow 3I^-(aq) + 2S_4O_6^{2-}(aq) \tag{11.4.57}$$

An oxidizing titrant such as MnO_4^-, Ce^{4+}, $Cr_2O_7^{2-}$, and I_3^-, is used when the titrand is in a reduced state. If the titrand is in an oxidized state, we can first reduce it with an auxiliary reducing agent and then complete the titration using an oxidizing titrant. Alternatively, we can titrate it using a reducing titrant. Iodide is a relatively strong reducing agent that could serve as a reducing titrant except that a solution of I– is susceptible to the air-oxidation of I^- to I_3^-.

$$3I^-(aq) \rightleftharpoons I_3^-(aq) + 2e^- \tag{11.4.58}$$

Note

A freshly prepared solution of KI is clear, but after a few days it may show a faint yellow coloring due to the presence of I_3^-.

Instead, adding an excess of KI reduces the titrand, releasing a stoichiometric amount of I_3^-. The amount of I_3^- produced is then determined by a back titration using thiosulfate, $S_2O_3^{2-}$, as a reducing titrant.

$$2S_2O_3^{2-}(aq) \rightleftharpoons 2S_4O_6^{2-}(aq) + 2e^- \tag{11.4.59}$$

Solutions of $S_2O_3^{2-}$ are prepared using $Na_2S_2O_3 \cdot 5H_2O$, and must be standardized before use. Standardization is accomplished by dissolving a carefully weighed portion of the primary standard KIO_3 in an acidic solution containing an excess of KI. The reaction between IO_3^- and I^-

$$IO_3^-(aq) + 8I^-(aq) + 6H^+(aq) \rightarrow 3\,I_3^-(aq) + 3H_2O(l) \tag{11.4.60}$$

liberates a stoichiometric amount of I_3^-. By titrating this I_3^- with thiosulfate, using starch as a visual indicator, we can determine the concentration of $S_2O_3^{2-}$ in the titrant.

Note

The standardization titration is

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightarrow 3I^-(aq) + 2S_4O_6^{2-}(aq) \tag{11.4.61}$$

which is the same reaction used to standardize solutions of I_3^-. This approach to standardizing solutions of $S_2O_3^{2-}$. is similar to the determination of the total chlorine residual outlined in Representative Method 9.3.

Although thiosulfate is one of the few reducing titrants that is not readily oxidized by contact with air, it is subject to a slow decomposition to bisulfite and elemental sulfur. If used over a period of several weeks, a solution of thiosulfate should be restandardized periodically. Several forms of bacteria are able to metabolize thiosulfate, which also can lead to a change in its concentration. This problem can be minimized by adding a preservative such as HgI_2 to the solution.

Another useful reducing titrant is ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, in which iron is present in the +2 oxidation state. A solution of Fe^{2+} is susceptible to air-oxidation, but when prepared in 0.5 M H_2SO_4 it remains stable for as long as a month. Periodic restandardization with $K_2Cr_2O_7$ is advisable. The titrant can be used to directly titrate the titrand by oxidizing Fe^{2+} to Fe^{3+}.

Alternatively, ferrous ammonium sulfate is added to the titrand in excess and the quantity of Fe^{3+} produced determined by back titrating with a standard solution of Ce^{4+} or $Cr_2O_7^{2-}$.

Inorganic Analysis

One of the most important applications of redox titrimetry is evaluating the chlorination of public water supplies. Representative Method 9.3, for example, describes an approach for determining the total chlorine residual by using the oxidizing power of chlorine to oxidize I^- to I_3^-. The amount of I_3^- is determined by back titrating with $S_2O_3^{2-}$.

The efficiency of chlorination depends on the form of the chlorinating species. There are two contributions to the total chlorine residual—the free chlorine residual and the combined chlorine residual. The free chlorine residual includes forms of chlorine that are available for disinfecting the water supply. Examples of species contributing to the free chlorine residual include Cl_2, HOCl and OCl^-. The combined chlorine residual includes those species in which chlorine is in its reduced form and, therefore, no longer capable of providing disinfection. Species contributing to the combined chlorine residual are NH_2Cl, $NHCl_2$ and NCl_3.

When a sample of iodide-free chlorinated water is mixed with an excess of the indicator *N*,*N*-diethyl-*p*-phenylenediamine (DPD), the free chlorine oxidizes a stoichiometric portion of DPD to its red-colored form. The oxidized DPD is then back titrated to its colorless form using ferrous ammonium sulfate as the titrant. The volume of titrant is proportional to the free residual chlorine.

Having determined the free chlorine residual in the water sample, a small amount of KI is added, catalyzing the reduction monochloramine, NH_2Cl, and oxidizing a portion of the DPD back to its red-colored form. Titrating the oxidized DPD with ferrous ammonium sulfate yields the amount of NH_2Cl in the sample. The amount of dichloramine and trichloramine are determined in a similar fashion.

The methods described above for determining the total, free, or combined chlorine residual also are used to establish a water supply's chlorine demand. Chlorine demand is defined as the quantity of chlorine needed to completely react with any substance that can be oxidized by chlorine, while also maintaining the desired chlorine residual. It is determined by adding progressively greater amounts of chlorine to a set of samples drawn from the water supply and determining the total, free, or combined chlorine residual.

Another important example of redox titrimetry, which finds applications in both public health and environmental analyses is the determination of dissolved oxygen. In natural waters, such as lakes and rivers, the level of dissolved O_2 is important for two reasons: it is the most readily available oxidant for the biological oxidation of inorganic and organic pollutants; and it is necessary for the support of aquatic life. In a wastewater treatment plant dissolved O_2 is essential for the aerobic oxidation of waste materials. If the concentration of dissolved O_2 falls below a critical value, aerobic bacteria are replaced by anaerobic bacteria, and the oxidation of organic waste produces undesirable gases, such as CH_4 and H_2S.

One standard method for determining the dissolved O_2 content of natural waters and wastewaters is the Winkler method. A sample of water is collected without exposing it to the atmosphere, which might change the concentration of dissolved O_2. The sample is first treated with a solution of $MnSO_4$, and then with a solution of NaOH and KI. Under these alkaline conditions the dissolved oxygen oxidizes Mn^{2+} to MnO_2.

$$2Mn^{2+}(aq) + 4OH^-(aq) + O_2(g) \rightarrow 2MnO_2(s) + 2H_2O(l) \tag{11.4.62}$$

After the reaction is complete, the solution is acidified with H_2SO_4. Under the now acidic conditions I^- is oxidized to I_3^- by MnO_2.

$$MnO_2(s) + 3I^-(aq) + 4H^+(aq) \rightarrow Mn^{2+} + I_3^-(aq) + 2H_2O(l) \tag{11.4.63}$$

The amount of I_3^- formed is determined by titrating with $S_2O_3^{2-}$ using starch as an indicator. The Winkler method is subject to a variety of interferences, and several modifications to the original procedure have been proposed. For example, NO_2^- interferes because it can reduce I_3^- to I^- under acidic conditions. This interference is eliminated by adding sodium azide, NaN_3, reducing NO_2^- to N_2. Other reducing agents, such as Fe^{2+}, are eliminated by pretreating the sample with $KMnO_4$, and destroying the excess permanganate with $K_2C_2O_4$.

Another important example of redox titrimetry is the determination of water in nonaqueous solvents. The titrant for this analysis is known as the Karl Fischer reagent and consists of a mixture of iodine, sulfur dioxide, pyridine, and methanol. Because the concentration of pyridine is sufficiently large, I_2 and SO_2 react with pyridine (py) to form the complexes py•I_2 and py•SO_2. When added to a sample containing water, I_2 is reduced to I^- and SO_2 is oxidized to SO_3.

$$py \bullet I_2 + py \bullet SO_2 + py + H_2O \rightarrow 2py \bullet HI + py \bullet SO_3 \tag{11.4.64}$$

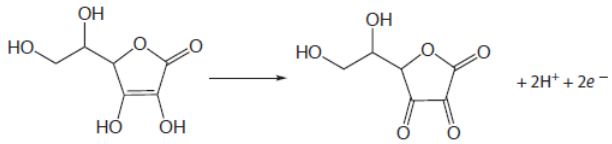
Methanol is included to prevent the further reaction of py•SO_3 with water. The titration's end point is signaled when the solution changes from the product's yellow color to the brown color of the Karl Fischer reagent.

Organic Analysis

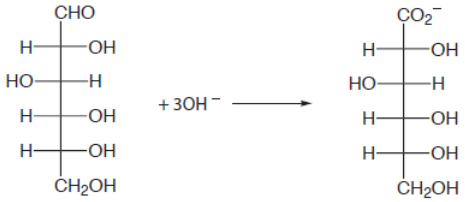
Redox titrimetry also is used for the analysis of organic analytes. One important example is the determination of the chemical oxygen demand (COD) of natural waters and wastewaters. The COD provides a measure of the quantity of oxygen necessary to completely oxidize all the organic matter in a sample to CO_2 and H_2O. Because no attempt is made to correct for organic matter that can not be decomposed biologically, or for slow decomposition kinetics, the COD always overestimates a sample's true oxygen demand. The determination of COD is particularly important in managing industrial wastewater treatment facilities where it is used to monitor the release of organic-rich wastes into municipal sewer systems or the environment.

A sample's COD is determined by refluxing it in the presence of excess $K_2Cr_2O_7$, which serves as the oxidizing agent. The solution is acidified with H_2SO_4 using Ag_2SO_4 to catalyze the oxidation of low molecular weight fatty acids. Mercuric sulfate, $HgSO_4$, is added to complex any chloride that is present, preventing the precipitation of the Ag^+ catalyst as AgCl. Under these conditions, the efficiency for oxidizing organic matter is 95–100%. After refluxing for two hours, the solution is cooled to room temperature and the excess $Cr_2O_7^{2-}$ is determined by back titrating using ferrous ammonium sulfate as the titrant and ferroin as the indicator. Because it is difficult to completely remove all traces of organic matter from the reagents, a blank titration must be performed. The difference in the amount of ferrous ammonium sulfate needed to titrate the sample and the blank is proportional to the COD.

Iodine has been used as an oxidizing titrant for a number of compounds of pharmaceutical interest. Earlier we noted that the reaction of $S_2O_3^{2-}$ with I_3^- produces the tetrathionate ion, $S_4O_6^{2-}$. The tetrathionate ion is actually a dimer consisting of two thiosulfate ions connected through a disulfide (–S–S–) linkage. In the same fashion, I_3^- can be used to titrate mercaptans of the general formula RSH, forming the dimer RSSR as a product. The amino acid cysteine also can be titrated with I_3^-. The product of this titration is cystine, which is a dimer of cysteine. Triiodide also can be used for the analysis of ascorbic acid (vitamin C) by oxidizing the enediol functional group to an alpha diketone



and for the analysis of reducing sugars, such as glucose, by oxidizing the aldehyde functional group to a carboxylate ion in a basic solution.



An organic compound containing a hydroxyl, a carbonyl, or an amine functional group adjacent to an hydoxyl or a carbonyl group can be oxidized using metaperiodate, IO_4^-, as an oxidizing titrant.

$$IO_4^-(aq) + H_2O(l) + 2e^- \rightleftharpoons IO_3^-(aq) + 2OH^-(aq) \qquad (11.4.65)$$

A two-electron oxidation cleaves the C–C bond between the two functional groups, with hydroxyl groups being oxidized to aldehydes or ketones, carbonyl functional groups being oxidized to carboxylic acids, and amines being oxidized to an aldehyde and an amine (ammonia if a primary amine). The analysis is conducted by adding a known excess of IO_4^- to the solution containing the analyte, and allowing the oxidation to take place for approximately one hour at room temperature. When the oxidation is complete, an excess of KI is added, which converts any unreacted IO_4^- to IO_3^- and I_3^-.

$$IO_4^-(aq) + 3I^-(aq) + H_2O(l) \rightarrow IO_3^-(aq) + I_3^-(aq) + 2OH^-(aq) \qquad (11.4.66)$$

The I_3^- is then determined by titrating with $S_2O_3^{2-}$ using starch as an indicator.

Quantitative Calculations

The quantitative relationship between the titrand and the titrant is determined by the stoichiometry of the titration reaction. If you are unsure of the balanced reaction, you can deduce the stoichiometry by remembering that the electrons in a redox reaction must be conserved.

Example 9.11

The amount of Fe in a 0.4891-g sample of an ore was determined by titrating with $K_2Cr_2O_7$. After dissolving the sample in HCl, the iron was brought into the +2 oxidation state using a Jones reductor. Titration to the diphenylamine sulfonic acid end point required 36.92 mL of 0.02153 M $K_2Cr_2O_7$. Report the ore's iron content as %w/w Fe_2O_3.

(Although we can deduce the stoichiometry between the titrant and the titrand without balancing the titration reaction, the balanced reaction

$$K_2Cr_2O_7(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 2K^+(aq) + 6Fe^{3+}(aq) + 7H_2O(l) \quad (11.4.67)$$

does provide useful information. For example, the presence of H^+ reminds us that the reaction^fs feasibility is pH-dependent.)

Solution

Because we have not been provided with the titration reaction, let's use a conservation of electrons to deduce the stoichiometry. During the titration the analyte is oxidized from Fe^{2+} to Fe^{3+}, and the titrant is reduced from $Cr_2O_7^{2-}$ to Cr^{3+}. Oxidizing Fe^{2+} to Fe^{3+} requires only a single electron. Reducing $Cr_2O_7^{2-}$, in which each chromium is in the +6 oxidation state, to Cr^{3+} requires three electrons per chromium, for a total of six electrons. A conservation of electrons for the titration, therefore, requires that each mole of $K_2Cr_2O_7$ reacts with six moles of Fe^{2+}.

The moles of $K_2Cr_2O_7$ used in reaching the end point is

$$(0.02153\ \text{M}\ K_2Cr_2O_7) \times (0.03692\ \text{L}\ K_2Cr_2O_7) = 7.949 \times 10^{-4}\ \text{mol}\ K_2Cr_2O_7 \quad (11.4.68)$$

which means that the sample contains

$$7.949 \times 10^{-4}\ \text{mol}\ K_2Cr_2O_7 \times \frac{6\ \text{mol}\ Fe^{2+}}{\text{mol}\ K_2Cr_2O_7} = 4.769 \times 10^{-3}\ \text{mol}\ Fe^{2+} \quad (11.4.69)$$

Thus, the %w/w Fe_2O_3 in the sample of ore is

$$4.769 \times 10^{-3}\ \text{mol}\ Fe^{2+} \times \frac{1\ \text{mol}\ Fe_2O_3}{2\ \text{mol}\ Fe^{2+}} \times \frac{159.69\ \text{g}\ Fe_2O_3}{\text{mol}\ Fe_2O_3} = 0.3808\ \text{g}\ Fe_2O_3 \quad (11.4.70)$$

$$\frac{0.3808\ \text{g}\ Fe_2O_3}{0.4891\ \text{g sample}} \times 100 = 77.86\%\ \text{w/w}\ Fe_2O_3 \quad (11.4.71)$$

Practice Exercise 9.20

The purity of a sample of sodium oxalate, $Na_2C_2O_4$, is determined by titrating with a standard solution of $KMnO_4$. If a 0.5116-g sample requires 35.62 mL of 0.0400 M $KMnO_4$ to reach the titration's end point, what is the %w/w $Na_2C_2O_4$ in the sample.

Click here to review your answer to this exercise.

As shown in the following two examples, we can easily extend this approach to an analysis that requires an indirect analysis or a back titration.

Example 9.12

A 25.00-mL sample of a liquid bleach was diluted to 1000 mL in a volumetric flask. A 25-mL portion of the diluted sample was transferred by pipet into an Erlenmeyer flask containing an excess of KI, reducing the OCl^- to Cl^-, and producing I_3^-. The liberated I_3^- was determined by titrating with 0.09892 M $Na_2S_2O_3$, requiring 8.96 mL to reach the starch indicator end point. Report the %w/v NaOCl in the sample of bleach.

Solution

To determine the stoichiometry between the analyte, NaOCl, and the titrant, $Na_2S_2O_3$, we need to consider both the reaction between OCl^- and I^-, and the titration of I_3^- with $Na_2S_2O_3$.

First, in reducing OCl^- to Cl^-, the oxidation state of chlorine changes from +1 to –1, requiring two electrons. The oxidation of three I^- to form I_3^- releases two electrons as the oxidation state of each iodine changes from –1 in I^- to –⅓ in I_3^-. A conservation of electrons, therefore, requires that each mole of OCl^- produces one mole of I_3^-.

Second, in the titration reaction, I_3^-. is reduced to I^- and $S_2O_3^{2-}$ is oxidized to $S_4O_6^{2-}$. Reducing I_3^- to $3I^-$ requires two elections as each iodine changes from an oxidation state of –⅓ to –1. In oxidizing $S_2O_3^{2-}$ to $S_4O_6^{2-}$, each sulfur changes its oxidation state from +2 to +2.5, releasing one electron for each $S_2O_3^{2-}$. A conservation of electrons, therefore, requires that each mole of I_3^- reacts with two moles of $S_2O_3^{2-}$.

Finally, because each mole of OCl^- produces one mole of I_3^-, and each mole of I_3^- reacts with two moles of $S_2O_3^{2-}$, we know that every mole of NaOCl in the sample ultimately results in the consumption of two moles of $Na_2S_2O_3$.

The balanced reactions for this analysis are:

$$OCl^-(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + Cl^-(aq) + H_2O(l) \tag{11.4.72}$$

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 3I^-(aq) \tag{11.4.73}$$

The moles of $Na_2S_2O_3$ used in reaching the titration's end point is

$$(0.09892\ \text{M}\ Na_2S_2O_3) \times (0.00896\ \text{L}\ Na_2S_2O_3) = 8.86 \times 10^{-4}\ \text{mol}\ Na_2S_2O_3 \tag{11.4.74}$$

which means the sample contains

$$8.86 \times 10^{-4}\ \text{mol}\ Na_2S_2O_3 \times \frac{1\ \text{mol NaOCl}}{2\ \text{mol}\ Na_2S_2O_3} \times \frac{74.44\ \text{g NaOCl}}{\text{mol NaOCl}} = 0.03299\ \text{g NaOCl} \tag{11.4.75}$$

Thus, the %w/v NaOCl in the diluted sample is

$$\frac{0.03299\ \text{g NaOCl}}{25.00\ \text{mL}} \times 100 = 0.132\%\ \text{w/v NaOCl} \tag{11.4.76}$$

Because the bleach was diluted by a factor of 40 (25 mL to 1000 mL), the concentration of NaOCl in the bleach is 5.28% (w/v).

Example 9.13

The amount of ascorbic acid, $C_6H_8O_6$, in orange juice was determined by oxidizing the ascorbic acid to dehydroascorbic acid, $C_6H_6O_6$, with a known amount of I_3^-, and back titrating the excess I_3^- with $Na_2S_2O_3$. A 5.00-mL sample of filtered orange juice was treated with 50.00 mL of 0.01023 M I_3^-. After the oxidation was complete, 13.82 mL of 0.07203 M $Na_2S_2O_3$ was needed to reach the starch indicator end point. Report the concentration ascorbic acid in mg/100 mL.

Solution

For a back titration we need to determine the stoichiometry between I_3^- and the analyte, $C_6H_8O_6$, and between I_3^- and the titrant, $Na_2S_2O_3$. The later is easy because we know from Example 9.12 that each mole of I_3^- reacts with two moles of $Na_2S_2O_3$.

The balanced reactions for this analysis are:

$$C_6H_8O_6(aq) + I_3^-(aq) \rightarrow 3I^-(aq) + C_6H_6O_6(aq) + 2H^+(aq) \tag{11.4.77}$$

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 3I^-(aq) \tag{11.4.78}$$

In oxidizing ascorbic acid to dehydroascorbic acid, the oxidation state of carbon changes from +⅔ in $C_6H_8O_6$ to +1 in $C_6H_6O_6$. Each carbon releases ⅓ of an electron, or a total of two electrons per ascorbic acid. As we learned in Example 9.12, reducing I_3^- requires two electrons; thus, a conservation of electrons requires that each mole of ascorbic acid consumes one mole of I_3^-.

The total moles of I_3^- reacting with $C_6H_8O_6$ and with $Na_2S_2O_3$ is

$$(0.01023\ \text{M}\ I_3^-) \times (0.05000\ \text{L}\ I_3^-) = 5.115 \times 10^{-4}\ \text{mol}\ I_3^- \tag{11.4.79}$$

The back titration consumes

$$0.01382\ \text{L}\ Na_2S_2O_3 \times \frac{0.07203\ \text{mol}\ Na_2S_2O_3}{\text{L}\ Na_2S_2O_3} \times \frac{1\ \text{mol}\ I_3^-}{2\ \text{mol}\ Na_2S_2O_3} = 4.977 \times 10^{-4}\ \text{mol}\ I_3^- \tag{11.4.80}$$

Subtracting the moles of I_3^- reacting with $Na_2S_2O_3$ from the total moles of I_3^- gives the moles reacting with ascorbic acid.

$$5.115 \times 10^{-4} \text{ mol } I_3^- - 4.977 \times 10^{-4} \text{ mol } I_3^- = 1.38 \times 10^{-5} \text{ mol } I_3^- \quad (11.4.81)$$

The grams of ascorbic acid in the 5.00-mL sample of orange juice is

$$1.38 \times 10^{-5} \text{ mol } I_3^- \times \frac{1 \text{ mol } C_6H_8O_6}{\text{mol } I_3^-} \times \frac{176.13 \text{ g } C_6H_8O_6}{\text{mol } C_6H_8O_6} = 2.43 \times 10^{-3} \text{ g } C_6H_8O_6 \quad (11.4.82)$$

There are 2.43 mg of ascorbic acid in the 5.00-mL sample, or 48.6 mg per 100 mL of orange juice.

Practice Exercise 9.21

A quantitative analysis for ethanol, C_2H_6O, can be accomplished by a redox back titration. Ethanol is oxidized to acetic acid, $C_2H_4O_2$, using excess dichromate, $Cr_2O_7^{2-}$, which is reduced to Cr^{3+}. The excess dichromate is titrated with Fe^{2+}, giving Cr^{3+} and Fe^{3+} as products. In a typical analysis, a 5.00-mL sample of a brandy is diluted to 500 mL in a volumetric flask. A 10.00-mL sample is taken and the ethanol is removed by distillation and collected in 50.00 mL of an acidified solution of 0.0200 M $K_2Cr_2O_7$. A back titration of the unreacted $Cr_2O_7^{2-}$ requires 21.48 mL of 0.1014 M Fe^{2+}. Calculate the %w/v ethanol in the brandy.

Click here to review your answer to this exercise.

9.4.4 Evaluation of Redox Titrimetry

The scale of operations, accuracy, precision, sensitivity, time, and cost of a redox titration are similar to those described earlier in this chapter for acid–base or a complexation titration. As with acid–base titrations, we can extend a redox titration to the analysis of a mixture of analytes if there is a significant difference in their oxidation or reduction potentials. Figure 9.42 shows an example of the titration curve for a mixture of Fe^{2+} and Sn^{2+} using Ce^{4+} as the titrant. A titration of a mixture of analytes is possible if their standard state potentials or formal potentials differ by at least 200 mV.

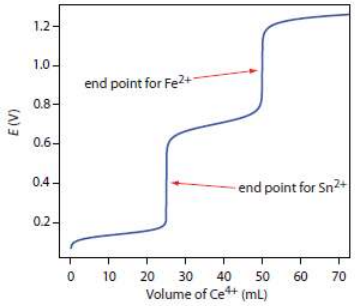


Figure 9.42 *Titration curve for the titration of 50.0 mL of 0.0125 M Sn^{2+} and 0.0250 M Fe^{2+} with 0.050 M Ce^{4+}. Both the titrand and the titrant are 1M in HCl.*

Contributors

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11.5: Phase Equilibrium in Solutions - Nonvolatile Solutes

Learning Objectives

- To describe the relationship between solute concentration and the physical properties of a solution.
- To understand that the total number of nonvolatile solute particles determines the decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus the pure solvent.

Many of the physical properties of solutions differ significantly from those of the pure substances discussed in earlier chapters, and these differences have important consequences. For example, the limited temperature range of liquid water (0°C–100°C) severely limits its use. Aqueous solutions have both a lower freezing point and a higher boiling point than pure water. Probably one of the most familiar applications of this phenomenon is the addition of ethylene glycol ("antifreeze") to the water in an automobile radiator. This solute lowers the freezing point of the water, preventing the engine from cracking in very cold weather from the expansion of pure water on freezing. Antifreeze also enables the cooling system to operate at temperatures greater than 100°C without generating enough pressure to explode.

Changes in the freezing point and boiling point of a solution depend primarily on the number of solute particles present rather than the kind of particles. Such properties of solutions are called colligative properties (from the Latin *colligatus*, meaning "bound together" as in a quantity). As we will see, the vapor pressure and osmotic pressure of solutions are also colligative properties.

Counting Concentrations and Effective Concentrations

When we determine the number of particles in a solution, it is important to remember that not all solutions with the same molarity contain the same concentration of solute particles. Consider, for example, 0.01 M aqueous solutions of sucrose, NaCl, and $\mathrm{CaCl_2}$. Because sucrose dissolves to give a solution of neutral molecules, the concentration of solute particles in a 0.01 M sucrose solution is 0.01 M. In contrast, both NaCl and $\mathrm{CaCl_2}$ are ionic compounds that dissociate in water to yield solvated ions. As a result, a 0.01 M aqueous solution of NaCl contains 0.01 M $\mathrm{Na^+}$ ions and 0.01 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.02 M. Similarly, the $\mathrm{CaCl_2}$ solution contains 0.01 M $\mathrm{Ca^{2+}}$ ions and 0.02 M $\mathrm{Cl^-}$ ions, for a total particle concentration of 0.03 M. These values are correct for dilute solutions, where the dissociation of the compounds to form separately solvated ions is complete.

At **higher concentrations** (typically >1 M), especially with salts of small, highly charged ions (such as $\mathrm{Mg^{2+}}$ or $\mathrm{Al^{3+}}$), or in solutions with less polar solvents, dissociation to give separate ions is often incomplete. The sum of the concentrations of the dissolved solute particles dictates the physical properties of a solution. In the following discussion, we must therefore keep the chemical nature of the solute firmly in mind. A greater discussion of this is below.

Vapor Pressure of Solutions and Raoult's Law For Nonvolatile Solutes

Adding a nonvolatile solute, one whose vapor pressure is too low to measure readily, to a volatile solvent decreases the vapor pressure of the solvent. We can understand this phenomenon qualitatively by examining Figure 11.5.1, which is a schematic diagram of the surface of a solution of glucose in water. In an aqueous solution of glucose, a portion of the surface area is occupied by nonvolatile glucose molecules rather than by volatile water molecules. As a result, fewer water molecules can enter the vapor phase per unit time, even though the surface water molecules have the same kinetic energy distribution as they would in pure water. At the same time, the rate at which water molecules in the vapor phase collide with the surface and reenter the solution is unaffected. The net effect is to shift the dynamic equilibrium between water in the vapor and the liquid phases, decreasing the vapor pressure of the solution compared with the vapor pressure of the pure solvent.

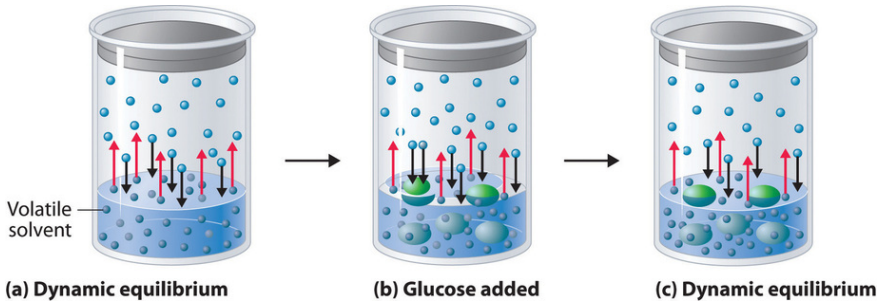


Figure 11.5.1: A Model Depicting Why the Vapor Pressure of a Solution of Glucose Is Less Than the Vapor Pressure of Pure Water. (a) When water or any volatile solvent is in a closed container, water molecules move into and out of the liquid phase at the same rate in a dynamic equilibrium. (b) If a nonvolatile solute such as glucose is added, some fraction of the surface area is occupied by solvated solute molecules. As a result, the rate at which water molecules evaporate is decreased, although initially their rate of condensation is unchanged. (c) When the glucose solution reaches equilibrium, the concentration of water molecules in the vapor phase, and hence the vapor pressure, is less than that of pure water. (CC BY-NC-SA; anonymous)

Figure 11.5.2 shows two beakers, one containing pure water and one containing an aqueous glucose solution, in a sealed chamber. We can view the system as having two competing equilibria: water vapor will condense in both beakers at the same rate, but water molecules will evaporate more slowly from the glucose solution because fewer water molecules are at the surface. Eventually all of the water will evaporate from the beaker containing the liquid with the higher vapor pressure (pure water) and condense in the beaker containing the liquid with the lower vapor pressure (the glucose solution). If the system consisted of only a beaker of water inside a sealed container, equilibrium between the liquid and vapor would be achieved rather rapidly, and the amount of liquid water in the beaker would remain constant.

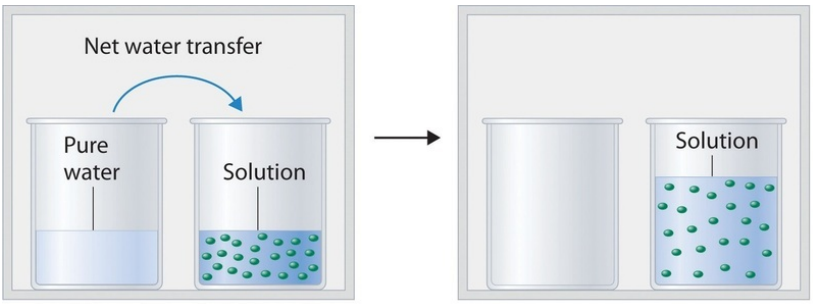


Figure 11.5.2: Transfer of Water to a Beaker Containing a Glucose Solution. (top) One beaker contains an aqueous solution of glucose, and the other contains pure water. If they are placed in a sealed chamber, the lower vapor pressure of water in the glucose solution results in a net transfer of water from the beaker containing pure water to the beaker containing the glucose solution. (bottom) Eventually, all of the water is transferred to the beaker that has the glucose solution. (CC BY-NC-SA; anonymous)

If the particles of a solute are essentially the same size as those of the solvent and both solute and solvent have roughly equal probabilities of being at the surface of the solution, then the effect of a solute on the vapor pressure of the solvent is proportional to the number of sites occupied by solute particles at the surface of the solution. Doubling the concentration of a given solute causes twice as many surface sites to be occupied by solute molecules, resulting in twice the decrease in vapor pressure. The relationship between solution composition and vapor pressure is therefore

$$P_A = \chi_A P_A^0 \tag{11.5.1}$$

where P_A is the vapor pressure of component A of the solution (in this case the solvent), χ_A is the mole fraction of A in solution, and P_A^0 is the vapor pressure of pure A. Equation 11.5.1 is known as **Raoult's law**, after the French chemist who developed it. If the solution contains only a single nonvolatile solute (B), then we can relate the mole fraction of the solvent to the solute

$$\chi_A + \chi_B = 1$$

and we can substitute $\chi_A = 1 - \chi_B$ into Equation 11.5.1 to obtain

$$\begin{aligned} P_A &= (1 - \chi_B) P_A^0 \\ &= P_A^0 - \chi_B P_A^0 \end{aligned}$$

Rearranging and defining $\Delta P_A = P_A^0 - P_A$, we obtain a relationship between the decrease in vapor pressure and the mole fraction of nonvolatile solute:

$$P_A^0 - P_A = \Delta P_A \tag{11.5.2}$$

$$= \chi_B P_A^0 \tag{11.5.3}$$

We can solve vapor pressure problems in either of two ways: by using Equation 11.5.1 to calculate the actual vapor pressure above a solution of a nonvolatile solute, or by using Equation 11.5.3 to calculate the decrease in vapor pressure caused by a specified amount of a nonvolatile solute.

Example 11.5.1: Anti-Freeze

Ethylene glycol ($HOCH_2CH_2OH$), the major ingredient in commercial automotive antifreeze, increases the boiling point of radiator fluid by lowering its vapor pressure. At 100°C, the vapor pressure of pure water is 760 mmHg. Calculate the vapor pressure of an aqueous solution containing 30.2% ethylene glycol by mass, a concentration commonly used in climates that do not get extremely cold in winter.

Given: identity of solute, percentage by mass, and vapor pressure of pure solvent

Asked for: vapor pressure of solution

Strategy:

A. Calculate the number of moles of ethylene glycol in an arbitrary quantity of water, and then calculate the mole fraction of water.
B. Use Raoult's law (Equation 11.5.1) to calculate the vapor pressure of the solution.

Solution:

A A 30.2% solution of ethylene glycol contains 302 g of ethylene glycol per kilogram of solution; the remainder (698 g) is water. To use Raoult's law to calculate the vapor pressure of the solution, we must know the mole fraction of water. Thus we must first calculate the number of moles of both ethylene glycol (EG) and water present:

$$moles\ EG = (302\ \cancel{g}) \left(\frac{1\ mol}{62.07\ \cancel{g}} \right) = 4.87\ mol\ EG$$

$$moles\ H_2O = (698\ \cancel{g}) \left(\frac{1\ mol}{18.02\ \cancel{g}} \right) = 38.7\ mol\ H_2O$$

The mole fraction of water is thus

$$\chi_{H_2O} = \frac{38.7\ \cancel{mol}\ H_2O}{38.7\ \cancel{mol}\ H_2O + 4.87\ \cancel{mol}\ EG} = 0.888$$

B From Raoult's law (Equation 11.5.1), the vapor pressure of the solution is

$$P_{H_2O} = (\chi_{H_2O})(P^0_{H_2O})$$

$$= (0.888)(760\ mmHg) = 675\ mmHg$$

Alternatively, we could solve this problem by calculating the mole fraction of ethylene glycol and then using Equation 11.5.3 to calculate the resulting decrease in vapor pressure:

$$\chi_{EG} = \frac{4.87\ mol\ EG}{4.87\ mol\ EG + 38.7\ mol\ H_2O}$$

$$= 0.112$$

$$\Delta P_{H_2O} = (\chi_{EG})(P^0_{H_2O})$$

$$= (0.112)(760\ mmHg) = 85.1\ mmHg$$

$$P_{H_2O} = P^0_{H_2O} - \Delta P_{H_2O} = 760\ mmHg - 85.1\ mmHg = 675\ mmHg$$

The same result is obtained using either method.

? Exercise 11.5.1

Seawater is an approximately 3.0% aqueous solution of NaCl by mass with about 0.5% of other salts by mass. Calculate the decrease in the vapor pressure of water at 25°C caused by this concentration of NaCl, remembering that 1 mol of NaCl produces 2 mol of solute particles. The vapor pressure of pure water at 25°C is 23.8 mmHg.

Answer

0.45 mmHg. This may seem like a small amount, but it constitutes about a 2% decrease in the vapor pressure of water and accounts in part for the higher humidity in the north-central United States near the Great Lakes, which are freshwater lakes. The decrease therefore has important implications for climate modeling.

Boiling Point Elevation

Recall that the normal boiling point of a substance is the temperature at which the vapor pressure equals 1 atm. If a nonvolatile solute lowers the vapor pressure of a solvent, it must also affect the boiling point. Because the vapor pressure of the solution at a given temperature is less than the vapor pressure of the pure solvent, achieving a vapor pressure of 1 atm for the solution requires a higher temperature than the normal boiling point of the solvent. Thus the boiling point of a solution is always greater than that of the pure solvent. We can see why this must be true by comparing the phase diagram for an aqueous solution with the phase diagram for pure water (Figure 11.5.4). The vapor pressure of the solution is less than that of pure water at all temperatures. Consequently, the liquid–vapor curve for the solution crosses the horizontal line corresponding to $P = 1\,atm$ at a higher temperature than does the curve for pure water.

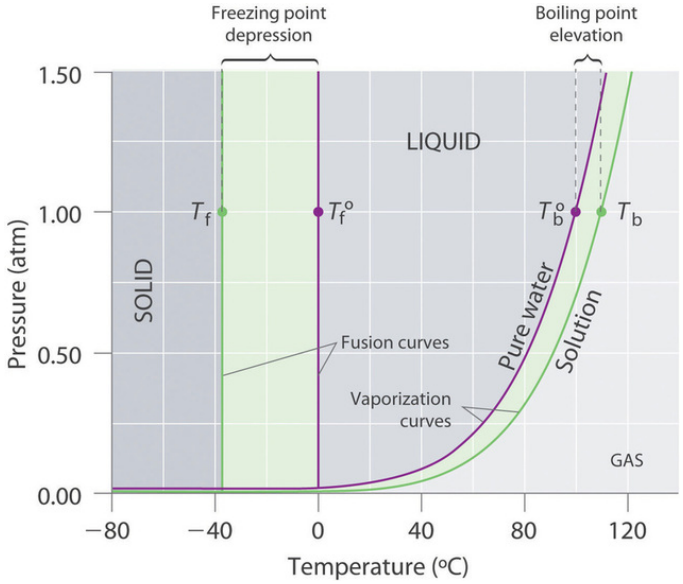


Figure 11.5.4: Phase Diagrams of Pure Water and an Aqueous Solution of a Nonvolatile Solute. The vaporization curve for the solution lies below the curve for pure water at all temperatures, which results in an increase in the boiling point and a decrease in the freezing point of the solution. (CC BY-NC-SA; anonymous)

> *The boiling point of a solution with a nonvolatile solute is **always** greater than the boiling point of the pure solvent.*

The magnitude of the increase in the boiling point is related to the magnitude of the decrease in the vapor pressure. As we have just discussed, the decrease in the vapor pressure is proportional to the concentration of the solute in the solution. Hence the magnitude of the increase in the boiling point must also be proportional to the concentration of the solute (Figure 11.5.5).

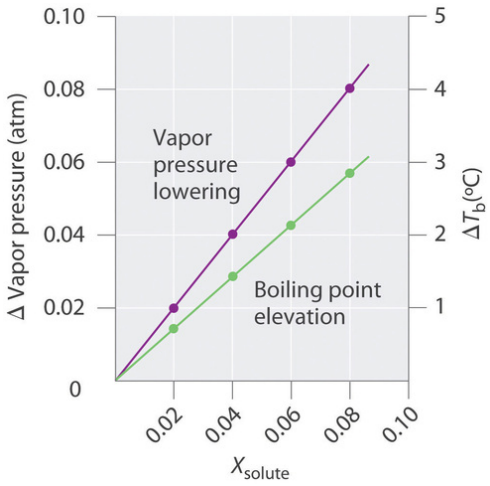


Figure 11.5.5: Vapor Pressure Decrease and Boiling Point Increase as Functions of the Mole Fraction of a Nonvolatile Solute. (CC BY-NC-SA; anonymous)

We can define the boiling point elevation (ΔT_b) as the difference between the boiling points of the solution and the pure solvent:

$$\Delta T_b = T_b - T_b^0 \tag{11.5.4}$$

where T_b is the boiling point of the solution and T_b^0 is the boiling point of the pure solvent. We can express the relationship between ΔT_b and concentration as follows

$$\Delta T_b = mK_b \tag{11.5.5}$$

where m is the concentration of the solute expressed in molality, and K_b is the **molal boiling point elevation constant** of the solvent, which has units of °C/m. Table 11.5.1 lists characteristic K_b values for several commonly used solvents. For relatively dilute solutions, the magnitude of both properties is proportional to the solute concentration.

Table 11.5.1: Boiling Point Elevation Constants (K_b) and Freezing Point Depression Constants (K_f) for Some Solvents

Solvent	Boiling Point (°C)	K_b (°C/m)	Freezing Point (°C)	K_f (°C/m)
acetic acid	117.90	3.22	16.64	3.63
benzene	80.09	2.64	5.49	5.07
d-(+)-camphor	207.4	4.91	178.8	37.8
carbon disulfide	46.2	2.42	−112.1	3.74
carbon tetrachloride	76.8	5.26	−22.62	31.4
chloroform	61.17	3.80	−63.41	4.60
nitrobenzene	210.8	5.24	5.70	6.87
water	100.00	0.51	0.00	1.86

The concentration of the solute is typically expressed as molality rather than mole fraction or molarity for two reasons. First, because the density of a solution changes with temperature, the value of molarity also varies with temperature. If the boiling point depends on the solute concentration, then by definition the system is not maintained at a constant temperature. Second, molality and mole fraction are proportional for relatively dilute solutions, but molality has a larger numerical value (a mole fraction can be only between zero and one). Using molality allows us to eliminate nonsignificant zeros.

According to Table 11.5.1, the molal boiling point elevation constant for water is 0.51°C/m. Thus a 1.00 m aqueous solution of a nonvolatile molecular solute such as glucose or sucrose will have an increase in boiling point of 0.51°C, to give a boiling point of 100.51°C at 1.00 atm. The increase in the boiling point of a 1.00 m aqueous NaCl solution will be approximately twice as large as that of the glucose or sucrose solution because 1 mol of NaCl produces 2 mol of dissolved ions. Hence a 1.00 m NaCl solution will have a boiling point of about 101.02°C.

Example 11.5.3

In Example 11.5.1, we calculated that the vapor pressure of a 30.2% aqueous solution of ethylene glycol at 100°C is 85.1 mmHg less than the vapor pressure of pure water. We stated (without offering proof) that this should result in a higher boiling point for the solution compared with pure water. Now that we have seen why this assertion is correct, calculate the boiling point of the aqueous ethylene glycol solution.

Given: composition of solution

Asked for: boiling point

Strategy:

Calculate the molality of ethylene glycol in the 30.2% solution. Then use Equation 11.5.5 to calculate the increase in boiling point.

Solution:

From Example 11.5.1, we know that a 30.2% solution of ethylene glycol in water contains 302 g of ethylene glycol (4.87 mol) per 698 g of water. The molality of the solution is thus

$$\text{molality of ethylene glycol} = \left(\frac{4.87\ mol}{698\ \cancel{g}\ H_2O}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right)$$
$$= 6.98\,m$$

From Equation 11.5.5, the increase in boiling point is therefore

$$\Delta T_b = mK_b$$
$$= (6.98\ \cancel{m})(0.51^\circ C/\ \cancel{m})$$
$$= 3.6^\circ C$$

The boiling point of the solution is thus predicted to be 104°C. With a solute concentration of almost 7 m, however, the assumption of a dilute solution used to obtain Equation 11.5.5 may not be valid.

Exercise 11.5.3

Assume that a tablespoon (5.00 g) of NaCl is added to 2.00 L of water at 20.0°C, which is then brought to a boil to cook spaghetti. At what temperature will the water boil?

Answer

100.04°C, or 100°C to three significant figures. (Recall that 1 mol of NaCl produces 2 mol of dissolved particles. The small increase in temperature means that adding salt to the water used to cook pasta has essentially no effect on the cooking time.)

Freezing Point Depression

The phase diagram in Figure 11.5.4 shows that dissolving a nonvolatile solute in water not only raises the boiling point of the water but also lowers its freezing point. The solid–liquid curve for the solution crosses the line corresponding to $P = 1\ atm$ at a lower temperature than the curve for pure water.

We can understand this result by imagining that we have a sample of water at the normal freezing point temperature, where there is a dynamic equilibrium between solid and liquid. Water molecules are continuously colliding with the ice surface and entering the solid phase at the same rate that water molecules are leaving the surface of the ice and entering the liquid phase. If we dissolve a nonvolatile solute such as glucose in the liquid, the dissolved glucose molecules will reduce the number of collisions per unit time between water molecules and the ice surface because some of the molecules colliding with the ice will be glucose. Glucose, though, has a very different structure than water, and it cannot fit into the ice lattice. Consequently, the presence of glucose molecules in the solution can only decrease the rate at which water molecules in the liquid collide with the ice surface and solidify. Meanwhile, the rate at which the water molecules leave the surface of the ice and enter the liquid phase is unchanged. The net

effect is to cause the ice to melt. The only way to reestablish a dynamic equilibrium between solid and liquid water is to lower the temperature of the system, which decreases the rate at which water molecules leave the surface of the ice crystals until it equals the rate at which water molecules in the solution collide with the ice.

By analogy to our treatment of boiling point elevation,the freezing point depression (ΔT_f) is defined as the difference between the freezing point of the pure solvent and the freezing point of the solution:

$$\Delta T_f = T_f^0 - T_f \tag{11.5.6}$$

where T_f^0 is the freezing point of the pure solvent and T_f is the freezing point of the solution.

The order of the terms is reversed compared with Equation 11.5.4 to express the freezing point depression as a positive number. The relationship between ΔT_f and the solute concentration is given by an equation analogous to Equation 11.5.5:

$$\Delta T_f = mK_f \tag{11.5.7}$$

where m is the molality of the solution and K_f is the molal freezing point depression constant for the solvent (in units of °C/m).

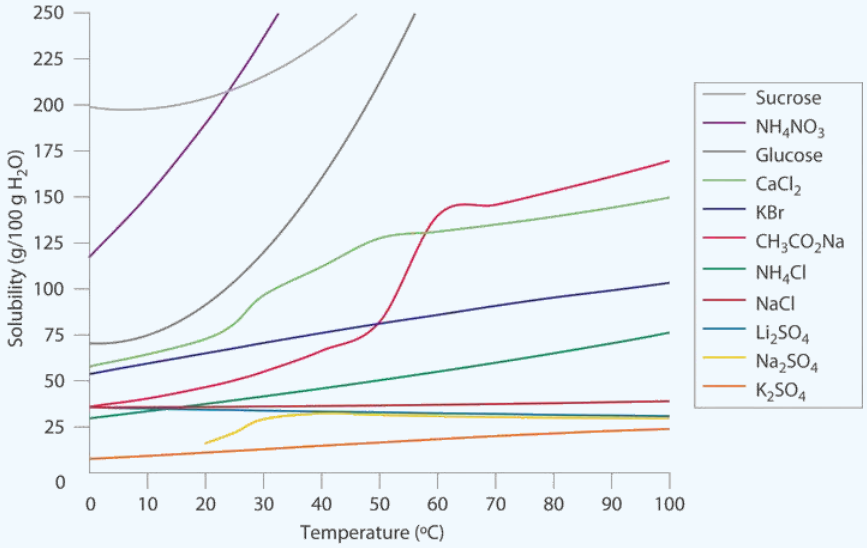
Like K_b, each solvent has a characteristic value of K_f (see Table 11.5.1). Freezing point depression depends on the total number of dissolved nonvolatile solute particles, just as with boiling point elevation. Thus an aqueous NaCl solution has twice as large a freezing point depression as a glucose solution of the same molality.

People who live in cold climates use freezing point depression to their advantage in many ways. For example, salt is used to melt ice and snow on roads and sidewalks, ethylene glycol is added to engine coolant water to prevent an automobile engine from being destroyed, and methanol is added to windshield washer fluid to prevent the fluid from freezing.

> The decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus a pure liquid all depend on the total number of dissolved nonvolatile solute particles.

Example 11.5.4: Salting the Roads

In colder regions of the United States, NaCl or $\mathrm{CaCl_2}$ 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 11.5.7 to calculate the freezing point depressions of the solutions.

Solution:

A. From Figure above, we can estimate the solubilities of NaCl and $\mathrm{CaCl_2}$ to be about 36 g and 60 g, respectively, per 100 g of water at 0°C. The corresponding concentrations in molality are

$$m_{NaCl} = \left(\frac{36\ \cancel{g\ NaCl}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ NaCl}{58.44\ \cancel{g\ NaCl}}\right)\left(\frac{1000\ \cancel{g}}{1\ kg}\right) = 6.2\ m$$

$$m_{CaCl_2} = \left(\frac{60\ \cancel{g\ CaCl_2}}{100\ \cancel{g}\ H_2O}\right)\left(\frac{1\ mol\ CaCl_2}{110.98\ \cancel{g\ CaCl_2}}\right)\left(\frac{1000\ \cancel{g}}{1kg}\right) = 5.4\ m$$

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 11.5.7:

$$\mathrm{NaCl}: \Delta T_f = mK_f = (12\ \cancel{m})(1.86^\circ C/\ \cancel{m}) = 22^\circ C$$

$$\mathrm{CaCl_2}: \Delta T_f = mK_f = (16\ \cancel{m})(1.86^\circ C/\ \cancel{m}) = 30^\circ C$$

Because the freezing point of pure water is 0°C, the actual freezing points of the solutions are −22°C and −30°C, respectively. Note that $\mathrm{CaCl_2}$ is substantially more effective at lowering the freezing point of water because its solutions contain three ions per formula unit. In fact, $\mathrm{CaCl_2}$ is the salt usually sold for home use, and it is also often used on highways.

Because the solubilities of both salts decrease with decreasing temperature, the freezing point can be depressed by only a certain amount, regardless of how much salt is spread on an icy road. If the temperature is significantly below the minimum temperature at which one of these salts will cause ice to melt (say −35°C), there is no point in using salt until it gets warmer

? Exercise 11.5.4

Calculate the freezing point of the 30.2% solution of ethylene glycol in water whose vapor pressure and boiling point we calculated in Examples 11.5.1 and 11.5.3

Answer

−13.0°C

✔ Example 11.5.5

Arrange these aqueous solutions in order of decreasing freezing points: 0.1 m KCl, 0.1 m glucose, 0.1 m $\mathrm{SrCl_2}$, 0.1 m ethylene glycol, 0.1 m benzoic acid, and 0.1 m HCl.

Given: molalities of six solutions

Asked for: relative freezing points

Strategy:

A. Identify each solute as a strong, weak, or nonelectrolyte, and use this information to determine the number of solute particles produced.

B. Multiply this number by the concentration of the solution to obtain the effective concentration of solute particles. The solution with the highest effective concentration of solute particles has the largest freezing point depression.

Solution:

A Because the molal concentrations of all six solutions are the same, we must focus on which of the substances are strong electrolytes, which are weak electrolytes, and which are nonelectrolytes to determine the actual numbers of particles in solution. KCl, $SrCl_2$, 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 > $SrCl_2$.

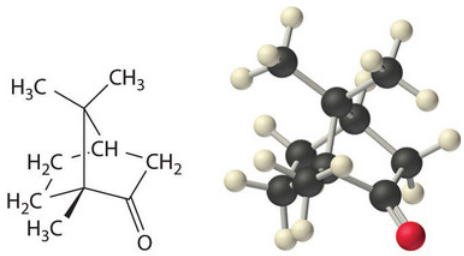
? Exercise 11.5.5

Arrange these aqueous solutions in order of increasing freezing points: 0.2 m NaCl, 0.3 m acetic acid, 0.1 m $CaCl_2$, and 0.2 m sucrose.

Answer

0.2 m NaCl (lowest freezing point) < 0.3 m acetic acid ≈ 0.1 m $CaCl_2$ < 0.2 m sucrose (highest freezing point)

Colligative properties can also be used to determine the molar mass of an unknown compound. One method that can be carried out in the laboratory with minimal equipment is to measure the freezing point of a solution with a known mass of solute. This method is accurate for dilute solutions (≤1% by mass) because changes in the freezing point are usually large enough to measure accurately and precisely. By comparing K_b and K_f values in Table 11.5.1, we see that changes in the boiling point are smaller than changes in the freezing point for a given solvent. Boiling point elevations are thus more difficult to measure precisely. For this reason, freezing point depression is more commonly used to determine molar mass than is boiling point elevation. Because of its very large value of K_f (37.8°C/m), d-(+)-camphor (Table 11.5.1) is often used to determine the molar mass of organic compounds by this method.



d-(+)-Camphor

✓ Example 11.5.6: Sulfur

A 7.08 g sample of elemental sulfur is dissolved in 75.0 g of CS_2 to create a solution whose freezing point is −113.5°C. Use these data to calculate the molar mass of elemental sulfur and thus the formula of the dissolved Sn molecules (i.e., what is the value of n?).

Given: masses of solute and solvent and freezing point

Asked for: molar mass and number of S atoms per molecule

Strategy:

A. Use Equation 11.5.6, the measured freezing point of the solution, and the freezing point of CS_2 from Table 11.5.1 to calculate the freezing point depression. Then use Equation 11.5.7 and the value of K_f from Table 11.5.1 to calculate the molality of the solution.

B. From the calculated molality, determine the number of moles of solute present.
C. Use the mass and number of moles of the solute to calculate the molar mass of sulfur in solution. Divide the result by the molar mass of atomic sulfur to obtain n, the number of sulfur atoms per mole of dissolved sulfur.

Solution:

A The first step is to calculate the freezing point depression using Equation 11.5.6:

$$\Delta T_f = T_f^0 - T_f = -112.1^\circ C - (-113.5^\circ C) = 1.4^\circ C$$

Then Equation 11.5.7 gives

$$m = \frac{\Delta T_f}{K_f} = \frac{1.4^\circ \cancel{C}}{3.74^\circ \cancel{C}/m} = 0.37\ m$$

B The total number of moles of solute present in the solution is

$$\text{moles solute} = \left(\frac{0.37 mol}{\cancel{kg}}\right)(75.0\ g)\left(\frac{1 kg}{1000\ g}\right) = 0.028\ mol$$

C We now know that 0.708 g of elemental sulfur corresponds to 0.028 mol of solute. The molar mass of dissolved sulfur is thus

$$\text{molar mass} = \frac{7.08\ g}{0.028\ mol} = 260\ g/mol$$

The molar mass of atomic sulfur is 32 g/mol, so there must be 260/32 = 8.1 sulfur atoms per mole, corresponding to a formula of S_8.

? Exercise 11.5.6

One of the byproducts formed during the synthesis of C_{60} is a deep red solid containing only carbon. A solution of 205 mg of this compound in 10.0 g of CCl_4 has a freezing point of −23.38°C. What are the molar mass and most probable formula of the substance?

Answer

847 g/mol; C_{70}

Osmotic Pressure

Osmotic pressure is a colligative property of solutions that is observed using a semipermeable membrane, a barrier with pores small enough to allow solvent molecules to pass through but not solute molecules or ions. The net flow of solvent through a semipermeable membrane is called osmosis (from the Greek osmós, meaning “push”). The direction of net solvent flow is always from the side with the lower concentration of solute to the side with the higher concentration.

Osmosis can be demonstrated using a U-tube like the one shown in Figure 11.5.6, which contains pure water in the left arm and a dilute aqueous solution of glucose in the right arm. A net flow of water through the membrane occurs until the levels in the arms eventually stop changing, which indicates that equilibrium has been reached. The osmotic pressure (Π) of the glucose solution is the difference in the pressure between the two sides, in this case the heights of the two columns. Although the semipermeable membrane allows water molecules to flow through in either direction, the rate of flow is not the same in both directions because the concentration of water is not the same in the two arms. The net flow of water through the membrane can be prevented by applying a pressure to the right arm that is equal to the osmotic pressure of the glucose solution.

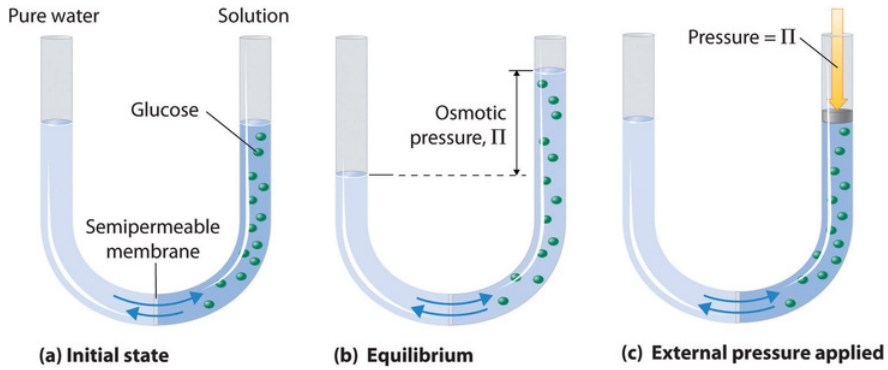


Figure 11.5.6: Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution (Π_{soln}), equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation. (CC BY-NC-SA; anonymous)

Just as with any other colligative property, the osmotic pressure of a solution depends on the concentration of dissolved solute particles. Osmotic pressure obeys a law that resembles the ideal gas equation:

$$\Pi = \frac{nRT}{V} = MRT \tag{11.5.8}$$

where M is the number of moles of solute per unit volume of solution (i.e., the molarity of the solution), R is the ideal gas constant, and T is the absolute temperature.

As shown in Example 11.5.7, osmotic pressures tend to be quite high, even for rather dilute solutions.

Example 11.5.7

When placed in a concentrated salt solution, certain yeasts are able to produce high internal concentrations of glycerol to counteract the osmotic pressure of the surrounding medium. Suppose that the yeast cells are placed in an aqueous solution containing 4.0% NaCl by mass; the solution density is 1.02 g/mL at 25°C.

a. Calculate the osmotic pressure of a 4.0% aqueous NaCl solution at 25°C.
b. If the normal osmotic pressure inside a yeast cell is 7.3 atm, corresponding to a total concentration of dissolved particles of 0.30 M, what concentration of glycerol must the cells synthesize to exactly balance the external osmotic pressure at 25°C?

Given: concentration, density, and temperature of NaCl solution; internal osmotic pressure of cell

Asked for: osmotic pressure of NaCl solution and concentration of glycerol needed

Strategy:

A. Calculate the molarity of the NaCl solution using the formula mass of the solute and the density of the solution. Then calculate the total concentration of dissolved particles.
B. Use Equation 11.5.8 to calculate the osmotic pressure of the solution.
C. Subtract the normal osmotic pressure of the cells from the osmotic pressure of the salt solution to obtain the additional pressure needed to balance the two. Use Equation 11.5.8 to calculate the molarity of glycerol needed to create this osmotic pressure.

Solution:

A The solution contains 4.0 g of NaCl per 100 g of solution. Using the formula mass of NaCl (58.44 g/mol) and the density of the solution (1.02 g/mL), we can calculate the molarity:

$$M_{NaCl} = \frac{moles\ NaCl}{\text{liter solution}}$$

$$= \left(\frac{4.0\ \cancel{g}\ NaCl}{58.44\ \cancel{g}/mol\ NaCl}\right)\left(\frac{1}{100\ \cancel{g\ solution}}\right)\left(\frac{1.02\ \cancel{g\ solution}}{1.00\ \cancel{mL}\ solution}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right)$$

$$= 0.70\ M\ \text{NaCl}$$

Because 1 mol of NaCl produces 2 mol of particles in solution, the total concentration of dissolved particles in the solution is (2)(0.70 M) = 1.4 M.

B Now we can use Equation 11.5.8 to calculate the osmotic pressure of the solution:

$$\Pi = MRT$$

$$= (1.4\ mol/L)\,[0.0821\ (L\cdot atm)/(K\cdot mol)]\,(298\ K)$$

$$= 34\ atm$$

C If the yeast cells are to exactly balance the external osmotic pressure, they must produce enough glycerol to give an additional internal pressure of (34 atm − 7.3 atm) = 27 atm. Glycerol is a nonelectrolyte, so we can solve Equation 11.5.8 for the molarity corresponding to this osmotic pressure:

$$M = \frac{\Pi}{RT}$$

$$= \frac{27\ \cancel{atm}}{[0.0821(L\cdot\ \cancel{atm})/(\ \cancel{K}\cdot mol)](298\ \cancel{K})}$$

$$= 1.1\ M\ \text{glycerol}$$

In solving this problem, we could also have recognized that the only way the osmotic pressures can be the same inside the cells and in the solution is if the concentrations of dissolved particles are the same. We are given that the normal concentration of dissolved particles in the cells is 0.3 M, and we have calculated that the NaCl solution is effectively 1.4 M in dissolved particles. The yeast cells must therefore synthesize enough glycerol to increase the internal concentration of dissolved particles from 0.3 M to 1.4 M—that is, an additional 1.1 M concentration of glycerol.

? Exercise 11.5.7

Assume that the fluids inside a sausage are approximately 0.80 M in dissolved particles due to the salt and sodium nitrite used to prepare them. Calculate the osmotic pressure inside the sausage at 100°C to learn why experienced cooks pierce the semipermeable skin of sausages before boiling them.

Answer

24 atm

Because of the large magnitude of osmotic pressures, osmosis is extraordinarily important in biochemistry, biology, and medicine. Virtually every barrier that separates an organism or cell from its environment acts like a semipermeable membrane, permitting the flow of water but not solutes. The same is true of the compartments inside an organism or cell. Some specialized barriers, such as those in your kidneys, are slightly more permeable and use a related process called dialysis, which permits both water and small molecules to pass through but not large molecules such as proteins.

The same principle has long been used to preserve fruits and their essential vitamins over the long winter. High concentrations of sugar are used in jams and jellies not for sweetness alone but because they greatly increase the osmotic pressure. Thus any bacteria not killed in the cooking process are dehydrated, which keeps them from multiplying in an otherwise rich medium for bacterial growth. A similar process using salt prevents bacteria from growing in ham, bacon, salt pork, salt cod, and other preserved meats. The effect of osmotic pressure is dramatically illustrated in Figure 11.5.7, which shows what happens when red blood cells are placed in a solution whose osmotic pressure is much lower or much higher than the internal pressure of the cells.

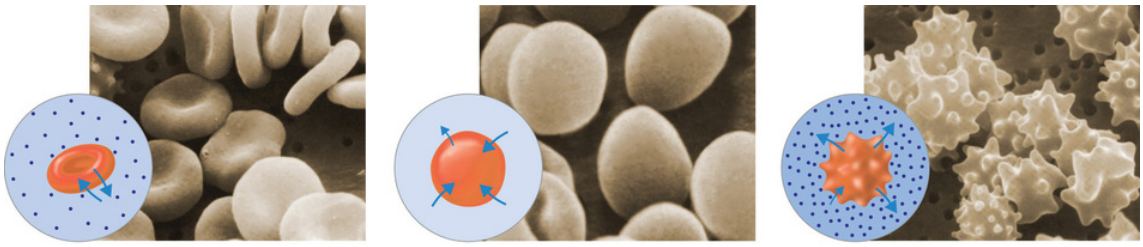


Figure 11.5.7: Effect on Red Blood Cells of the Surrounding Solution's Osmotic Pressure. (a) When red blood cells are placed in a dilute salt solution having the same osmotic pressure as the intracellular fluid, the rate of flow of water into and out of the cells is the same and their shape does not change. (b) When cells are placed in distilled water whose osmotic pressure is less than that of the intracellular fluid, the rate of flow of water into the cells is greater than the rate of flow out of the cells. The cells swell and eventually burst. (c) When cells are placed in a concentrated salt solution with an osmotic pressure greater than that of the intracellular fluid, the rate of flow of water out of the cells is greater than the rate of flow into the cells. The cells shrivel and become so deformed that they cannot function. (CC BY-NC-SA; anonymous)

In addition to capillary action, trees use osmotic pressure to transport water and other nutrients from the roots to the upper branches. Evaporation of water from the leaves results in a local increase in the salt concentration, which generates an osmotic pressure that pulls water up the trunk of the tree to the leaves.

Finally, a process called reverse osmosis can be used to produce pure water from seawater. As shown schematically in Figure 11.5.8, applying high pressure to seawater forces water molecules to flow through a semipermeable membrane that separates pure water from the solution, leaving the dissolved salt behind. Large-scale desalinization plants that can produce hundreds of thousands of gallons of freshwater per day are common in the desert lands of the Middle East, where they supply a large proportion of the freshwater needed by the population. Similar facilities are now being used to supply freshwater in southern California. Small, hand-operated reverse osmosis units can produce approximately 5 L of freshwater per hour, enough to keep 25 people alive, and are now standard equipment on US Navy lifeboats.

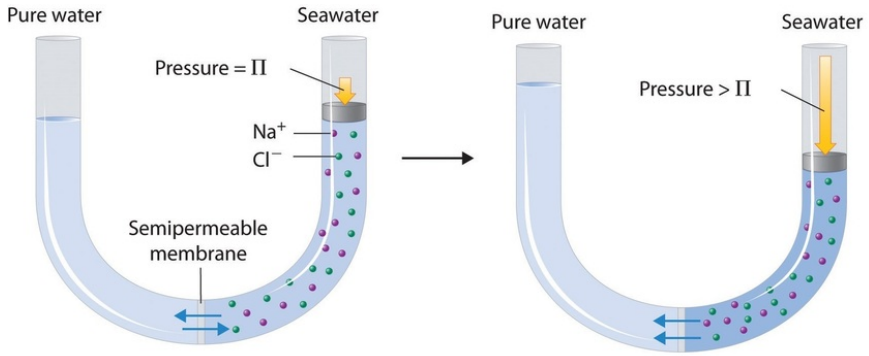


Figure 11.5.8: Desalinization of Seawater by Reverse Osmosis. (top) When the pressure applied to seawater equals its osmotic pressure (Π_{soln}), there is no net flow of water across the semipermeable membrane. (bottom) The application of pressure greater than the osmotic pressure of seawater forces water molecules to flow through the membrane, leaving behind a concentrated salt solution. In desalinization plants, seawater is continuously introduced under pressure and pure water is collected, so the process continues indefinitely. (CC BY-NC-SA; anonymous)

Colligative Properties of Electrolyte Solutions

Thus far we have assumed that we could simply multiply the molar concentration of a solute by the number of ions per formula unit to obtain the actual concentration of dissolved particles in an electrolyte solution. We have used this simple model to predict such properties as freezing points, melting points, vapor pressure, and osmotic pressure. If this model were perfectly correct, we would expect the freezing point depression of a 0.10 m solution of sodium chloride, with 2 mol of ions per mole of NaCl in solution, to be exactly twice that of a 0.10 m solution of glucose, with only 1 mol of molecules per mole of glucose in solution. In reality, this is not always the case. Instead, the observed change in freezing points for 0.10 m aqueous solutions of NaCl and KCl are significantly less than expected (−0.348°C and −0.344°C, respectively, rather than −0.372°C), which suggests that fewer particles than we expected are present in solution.

The relationship between the actual number of moles of solute added to form a solution and the apparent number as determined by colligative properties is called the van 't Hoff factor (i) and is defined as follows:

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}} \tag{11.5.9}$$

Named for Jacobus Hendricus van ’t Hoff (1852–1911), a Dutch chemistry professor at the University of Amsterdam who won the first Nobel Prize in Chemistry (1901) for his work on thermodynamics and solutions.

> *As the solute concentration increases, the van ’t Hoff factor decreases.*

The van ’t Hoff factor is therefore **a measure of a deviation from ideal behavior**. The lower the van ’t Hoff factor, the greater the deviation. As the data in Table 11.5.2 show, the van ’t Hoff factors for ionic compounds are somewhat lower than expected; that is, their solutions apparently contain fewer particles than predicted by the number of ions per formula unit. As the concentration of the solute increases, the van ’t Hoff factor decreases because ionic compounds generally do not totally dissociate in aqueous solution.

Table 11.5.2: van ’t Hoff Factors for 0.0500 M Aqueous Solutions of Selected Compounds at 25°C

Compound	i (measured)	i (ideal)
glucose	1.0	1.0
sucrose	1.0	1.0
$NaCl$	1.9	2.0
HCl	1.9	2.0
$MgCl_2$	2.7	3.0
$FeCl_3$	3.4	4.0
$Ca(NO_3)_2$	2.5	3.0
$AlCl_3$	3.2	4.0
$MgSO_4$	1.4	2.0

Instead, some of the ions exist as ion pairs, a cation and an anion that for a brief time are associated with each other without an intervening shell of water molecules (Figure 11.5.9). Each of these temporary units behaves like a single dissolved particle until it dissociates. Highly charged ions such as Mg^{2+}, Al^{3+}, SO_4^{2-}, and PO_4^{3-} have a greater tendency to form ion pairs because of their strong electrostatic interactions. The actual number of solvated ions present in a solution can be determined by measuring a colligative property at several solute concentrations.

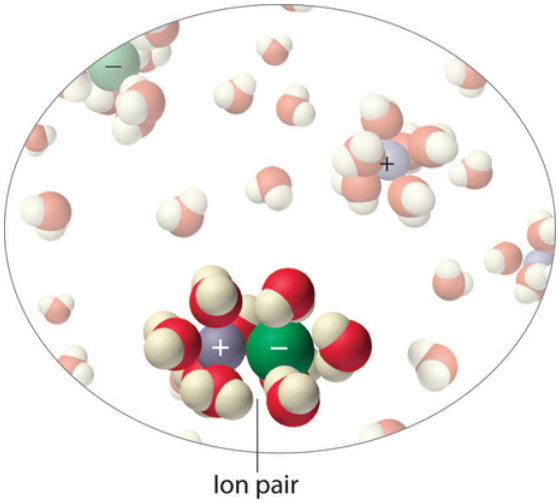


Figure 11.5.9: Ion Pairs. In concentrated solutions of electrolytes like $NaCl$, some of the ions form neutral ion pairs that are not separated by solvent and diffuse as single particles.

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Example 11.5.8: 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 11.5.8 to calculate the expected osmotic pressure of the solution based on the effective concentration of dissolved particles in the solvent.
B. Calculate the ratio of the observed osmotic pressure to the expected value. Multiply this number by the number of ions of solute per formula unit, and then use Equation 11.5.9 to calculate the van 't Hoff factor.

Solution:

A If $\mathrm{FeCl_3}$ 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 11.5.9, 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 11.5.8: 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**:

$$\Delta T_b = m K_b$$

- **freezing point depression:**

$$\Delta T_f = m K_f$$

- **osmotic pressure**:

$$\Pi = \frac{n}{V} RT = MRT$$

- **van ’t Hoff factor**:

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}}$$

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11.6: Phase Equilibrium in Solutions - Volatile Solutes

Learning Objectives

- To understand the relationship among temperature, pressure, and solubility.
- The understand that the solubility of a solid may increase or decrease with increasing temperature,
- To understand that the solubility of a gas decreases with an increase in temperature and a decrease in pressure.

Effect of Pressure on the Solubility of Gases: Henry's Law

External pressure has very little effect on the solubility of liquids and solids. In contrast, the solubility of gases increases as the partial pressure of the gas above a solution increases. This point is illustrated in Figure 11.6.1, which shows the effect of increased pressure on the dynamic equilibrium that is established between the dissolved gas molecules in solution and the molecules in the gas phase above the solution. Because the concentration of molecules in the gas phase increases with increasing pressure, the concentration of dissolved gas molecules in the solution at equilibrium is also higher at higher pressures.

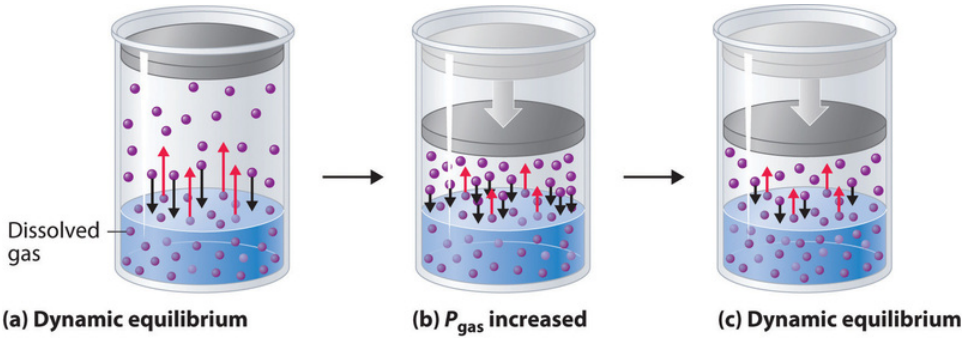


Figure 11.6.1: A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature. (a) When a gas comes in contact with a pure liquid, some of the gas molecules (purple spheres) collide with the surface of the liquid and dissolve. When the concentration of dissolved gas molecules has increased so that the rate at which gas molecules escape into the gas phase is the same as the rate at which they dissolve, a dynamic equilibrium has been established, as depicted here. This equilibrium is entirely analogous to the one that maintains the vapor pressure of a liquid. (b) Increasing the pressure of the gas increases the number of molecules of gas per unit volume, which increases the rate at which gas molecules collide with the surface of the liquid and dissolve. (c) As additional gas molecules dissolve at the higher pressure, the concentration of dissolved gas increases until a new dynamic equilibrium is established.

The relationship between pressure and the solubility of a gas is described quantitatively by Henry's law, which is named for its discoverer, the English physician and chemist, William Henry (1775–1836):

$$C = k_H P \tag{11.6.1}$$

where C is the concentration of dissolved gas at equilibrium, P is the partial pressure of the gas, and k_H is the Henry's law constant, which must be determined experimentally for each combination of gas, solvent, and temperature.

Although the gas concentration may be expressed in any convenient units, we will use molarity exclusively. The units of the Henry's law constant are therefore mol/(L·atm) = M/atm. Values of the Henry's law constants for solutions of several gases in water at 20°C are listed in Table 11.6.1.

As the data in Table 11.6.1 demonstrate, the concentration of a dissolved gas in water at a given pressure depends strongly on its physical properties. For a series of related substances, London dispersion forces increase as molecular mass increases. Thus among the elements of Group 18, the Henry's law constants increase smoothly from He to Ne to Ar. The table also shows that O_2 is almost twice as soluble as N_2. Although London dispersion forces are too weak to explain such a large difference, O_2 is paramagnetic and hence more polarizable than N_2, which explains its high solubility.

Table 11.6.1: Henry's Law Constants for Selected Gases in Water at 20°C

Gas	Henry's Law Constant [mol/(L·atm)] × 10^{-4}
Ar	15
CO_2	392

Gas	Henry's Law Constant [mol/(L·atm)] × 10^{-4}
H_2	8.1
He	3.9
N_2	7.1
Ne	4.7
O_2	14

Gases that react with the solvent do not obey Henry's law

Gases that react chemically with water, such as HCl and the other hydrogen halides, 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,

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

The dissociation of HCl into ions results in a much higher effective "solubility" than expected for a neutral molecule.

Jan 3, 2019, 5:36 PM

https://en.Wikipedia.org/wiki/Henry%...constants_Heff

https://www.sciencedirect.com/scienc...0469818690079X

https://www.atmos-chem-phys.net/15/4...-4399-2015.pdf

Henry's law has important applications. For example, bubbles of 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 N_2 from the air dissolves in the diver's internal fluids. If the diver ascends too quickly, the rapid pressure change causes small bubbles of 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 11.6.1: 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 11.6.1) to calculate the solubility, expressed as the concentration of dissolved gas.

Solution:

A According to Dalton's law, the partial pressure of O_2 is proportional to the mole fraction of O_2:

$$P_A = \chi_A P_t = (0.21)(1.00\ atm) = 0.21\ atm$$

B From Henry's law, the concentration of dissolved oxygen under these conditions is

$$CO_2 = k_H P_{O_2} = (1.27 \times 10^{-3}\ M/\ \cancel{atm})(0.21\ \ \cancel{atm}) = 2.7 \times 10^{-4}\ M$$

Exercise 11.6.1: Carbon Dioxide in Water

To understand why soft drinks "fizz" and then go "flat" after being opened, calculate the concentration of dissolved CO_2 in a soft drink:

a. bottled under a pressure of 5.0 atm of CO_2
b. in equilibrium with the normal partial pressure of CO_2 in the atmosphere (approximately $3 \times 10^{-4}\ atm$). The Henry's law constant for CO_2 in water at 25°C is $3.4 \times 10^{-2}\ M/atm$.

Answer a

0.17 M

Answer b

$1 \times 10^{-5} M$

Summary

The solubility of most substances depends strongly on the temperature and, in the case of gases, on the pressure. The solubility of most solid or liquid solutes increases with increasing temperature. The components of a mixture can often be separated using fractional crystallization, which separates compounds according to their solubilities. The solubility of a gas decreases with increasing temperature. Henry's law describes the relationship between the pressure and the solubility of a gas.

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11.7: Colloidal Suspensions

Learning Objectives

- To distinguish between true solutions and solutions with aggregate particles.

Suspensions and colloids are two common types of mixtures whose properties are in many ways intermediate between those of true solutions and heterogeneous mixtures. A suspension is a heterogeneous mixture of particles with diameters of about 1 µm (1000 nm) that are distributed throughout a second phase. Common suspensions include paint, blood, and hot chocolate, which are solid particles in a liquid, and aerosol sprays, which are liquid particles in a gas. If the suspension is allowed to stand, the two phases will separate, which is why paints must be thoroughly stirred or shaken before use. A colloid is also a heterogeneous mixture, but the particles of a colloid are typically smaller than those of a suspension, generally in the range of 2 to about 500 nm in diameter. Colloids include fog and clouds (liquid particles in a gas), milk (solid particles in a liquid), and butter (solid particles in a solid). Other colloids are used industrially as catalysts. Unlike in a suspension, the particles in a colloid do not separate into two phases on standing. The only combination of substances that cannot produce a suspension or a colloid is a mixture of two gases because their particles are so small that they always form true solutions. The properties of suspensions, colloids, and solutions are summarized in Table 11.7.1.

Table 11.7.1: Properties of Liquid Solutions, Colloids, and Suspensions

Type of Mixture	Approximate Size of Particles (nm)	Characteristic Properties	Examples
solution	< 2	not filterable; does not separate on standing; does not scatter visible light	air, white wine, gasoline, salt water
colloid	2–500	scatters visible light; translucent or opaque; not filterable; does not separate on standing	smoke, fog, ink, milk, butter, cheese
suspension	500–1000	cloudy or opaque; filterable; separates on standing	muddy water, hot cocoa, blood, paint

Colloids and Suspensions

Colloids were first characterized in about 1860 by Thomas Graham, who also gave us Graham's law of diffusion and effusion. Although some substances, such as starch, gelatin, and glue, appear to dissolve in water to produce solutions, Graham found that they diffuse very slowly or not at all compared with solutions of substances such as salt and sugar. Graham coined the word colloid (from the Greek kólla, meaning "glue") to describe these substances, as well as the words sol and gel to describe certain types of colloids in which all of the solvent has been absorbed by the solid particles, thus preventing the mixture from flowing readily, as we see in Jell-O. Two other important types of colloids are aerosols, which are dispersions of solid or liquid particles in a gas, and emulsions, which are dispersions of one liquid in another liquid with which it is immiscible.

Colloids share many properties with solutions. For example, the particles in both are invisible without a powerful microscope, do not settle on standing, and pass through most filters. However, the particles in a colloid scatter a beam of visible light, a phenomenon known as the Tyndall effect,The effect is named after its discoverer, John Tyndall, an English physicist (1820–1893). whereas the particles of a solution do not. The Tyndall effect is responsible for the way the beams from automobile headlights are clearly visible from the side on a foggy night but cannot be seen from the side on a clear night. It is also responsible for the colored rays of light seen in many sunsets, where the sun's light is scattered by water droplets and dust particles high in the atmosphere. An example of the Tyndall effect is shown in Figure 11.7.1.



Figure 11.7.1: Tyndall Effect, the Scattering of Light by Colloids (CC BY; LibreTexts)

Although colloids and suspensions can have particles similar in size, the two differ in stability: the particles of a colloid remain dispersed indefinitely unless the temperature or chemical composition of the dispersing medium is changed. The chemical explanation for the stability of colloids depends on whether the colloidal particles are hydrophilic or hydrophobic.

Most proteins, including those responsible for the properties of gelatin and glue, are hydrophilic because their exterior surface is largely covered with polar or charged groups. Starch, a long-branched polymer of glucose molecules, is also hydrophilic. A hydrophilic colloid particle interacts strongly with water, resulting in a shell of tightly bound water molecules that prevents the particles from aggregating when they collide. Heating such a colloid can cause aggregation because the particles collide with greater energy and disrupt the protective shell of solvent. Moreover, heat causes protein structures to unfold, exposing previously buried hydrophobic groups that can now interact with other hydrophobic groups and cause the particles to aggregate and precipitate from solution. When an egg is boiled, for example, the egg white, which is primarily a colloidal suspension of a protein called albumin, unfolds and exposes its hydrophobic groups, which aggregate and cause the albumin to precipitate as a white solid.

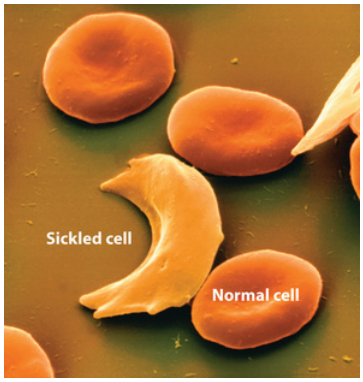


Figure 11.7.2: Sickle-Cell Anemia The characteristic shape of sickled red blood cells is the result of fibrous aggregation of hemoglobin molecules inside the cell.

A normal blood cell is circular in shape with a dimple in the middle, a sickled cell is banana shaped.

In some cases, a stable colloid can be transformed to an aggregated suspension by a minor chemical modification. Consider, for example, the behavior of hemoglobin, a major component of red blood cells. Hemoglobin molecules normally form a colloidal suspension inside red blood cells, which typically have a “donut” shape and are easily deformed, allowing them to squeeze through the capillaries to deliver oxygen to tissues. In a common inherited disease called sickle-cell anemia, one of the amino acids in hemoglobin that has a hydrophilic carboxylic acid side chain (glutamate) is replaced by another amino acid that has a hydrophobic side chain (valine). Under some conditions, the abnormal hemoglobin molecules can aggregate to form long, rigid fibers that cause the red blood cells to deform, adopting a characteristic sickle shape that prevents them from passing through the capillaries (Figure 11.7.2). The reduction in blood flow results in severe cramps, swollen joints, and liver damage. Until recently, many patients with sickle-cell anemia died before the age of 30 from infection, blood clots, or heart or kidney failure, although individuals with the sickle-cell genetic trait are more resistant to malaria than are those with “normal” hemoglobin.

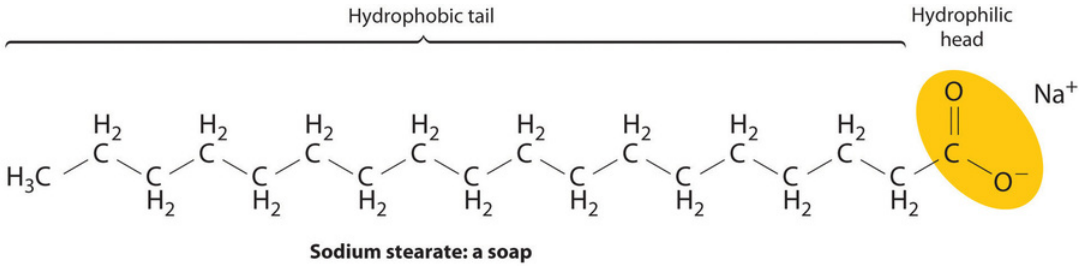


Figure 11.7.3: Formation of New Land by the Destabilization of a Colloid Suspension. This satellite photograph shows the Mississippi River delta from New Orleans (top) to the Gulf of Mexico (bottom). Where seawater mixes with freshwater from the Mississippi River, colloidal clay particles in the river water precipitate (tan area).

Aggregation and precipitation can also result when the outer, charged layer of a particle is neutralized by ions with the opposite charge. In inland waterways, clay particles, which have a charged surface, form a colloidal suspension. High salt concentrations in seawater neutralize the charge on the particles, causing them to precipitate and form land at the mouths of large rivers, as seen in the satellite view in Figure 11.7.3 Charge neutralization is also an important strategy for precipitating solid particles from gaseous colloids such as smoke, and it is widely used to reduce particulate emissions from power plants that burn fossil fuels.

Emulsions

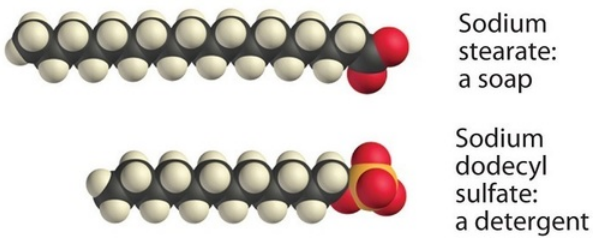
Emulsions are colloids formed by the dispersion of a hydrophobic liquid in water, thereby bringing two mutually insoluble liquids, such as oil and water, in close contact. Various agents have been developed to stabilize emulsions, the most successful being molecules that combine a relatively long hydrophobic "tail" with a hydrophilic "head":



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 11.7.4*a*).

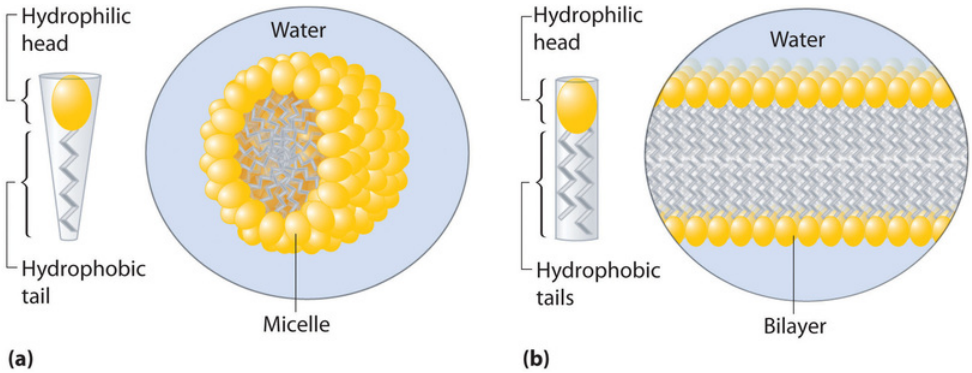
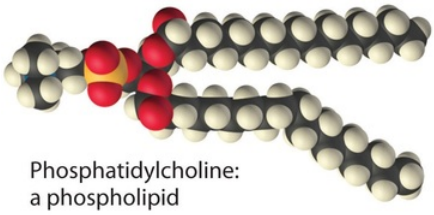


Figure 11.7.4: Micelles and a Phospholipid Bilayer. (a) Soaps and detergents, which contain a single hydrophobic tail on each molecule, form spherical micelles with the intertwined tails in the interior and the hydrophilic head groups on the exterior. (b) Phospholipids, which have two hydrophobic tails, tend to form extended double layers in which the hydrophobic tails are sandwiched between the hydrophilic head groups.

A large class of biological molecules called phospholipids consists of detergent-like molecules with a hydrophilic head and two hydrophobic tails, as can be seen in the molecule of phosphatidylcholine. The additional tail results in a cylindrical shape that prevents phospholipids from forming a spherical micelle. Consequently, phospholipids form bilayers, extended sheets consisting of a double layer of molecules. As shown in Figure 11.7.4*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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11.E: Solutions (Exercises)

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

Q.1

A student goes to the hospital and has blood work done and the results state that he has a bromide count of $3.17\,\frac{mg}{dL}$.

a. What is the molar concentration of the students blood?
b. What is the molality of the student's blood if the density of his blood was found to be $1.06\,\frac{g}{mL}$?
c. How much of the students blood would be require to get $3g$ of bromide?

Solution

The molar mass of bromide is $79.90\,\frac{g}{mol}$ $1L = 10dL$, $1g = 1000mg$

$$\left(\frac{3.17\ \cancel{mg}}{1\ \cancel{dL}}\right)\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{10\ \cancel{dL}}{1\text{L}}\right)\left(\frac{1\text{mol}}{79.90\ \cancel{g}}\right) = 3.97\times10^{-4}\ \frac{mol}{L}$$

Assume there is 1L of solution. Modality (m) is calculated by:

$$3.17\text{ x }10^{-2}\ \cancel{g}\left(\frac{1\text{ mol}}{79.90\ \cancel{g}}\right)\left(\frac{1}{1.06\text{ kg}}\right) = 3.74\times10^{-4}\,\frac{mol}{kg}$$

If we know that there is $3.17\times10^{-2}g$ of bromide in $1L$ of blood, so all that needs to be done is divide $3g$ by $3.17\times10^{-2}\ \frac{g}{L}$:
Volume of Blood = 94.64 L

Q.5

Given a 3.1416 M aqueous solution of sucrose, $C_{12}H_{22}O_{11}$ with a density of $1.5986\ \frac{\text{g}}{\text{mL}}$. Calculate the molality of this solution, remember that the molar mass of sucrose is $342.297\frac{\text{g}}{\text{mol}}$

Solution

Before we calculate the molality of this solution, don't forget that molarity is just mol/L so we will multiply the molarity of the solution by 1 L to isolate the moles.

$$1.00\ \cancel{L}\ \text{Water} = \frac{3.1416\ mol\ \text{Sucrose}}{1.00\ \cancel{L}\ \text{Water}} = 3.1416\ mol\ \text{Sucrose}$$

Once we have the moles of Sucrose we will multiply it by the molar mass of sucrose in order to find the number of sucrose grams present in the solution:

$$3.1416\ \cancel{mol}\ \text{Sucrose} = \frac{342.297\ g\ \text{Sucrose}}{1.00\ \cancel{mol}\ \text{Sucrose}} = 1075.4\ g\ \text{Sucrose}$$

We next will multiply the density by 1000 mL so as get the number of grams per liter, this way we can find the total grams of the solution and can subtract the sucrose grams from the solution grams to find the grams of water.

$$1000\ \cancel{mL}\ = \frac{1.5986\ g\ \text{SucroseSoln}}{1.00\ \cancel{mL}\ \text{SucroseSoln}} = 1598.6\ g/L\ \text{SucroseSoln}$$

$$\text{Water grams} = [1598.6g\ \text{Sucrose Soln.}] - [1075.4g\ \text{Sucrose}] = 523.2g\ \text{Water}\ = 0.5232\ kg\ \text{Water}$$

Lastly we divide the moles of Sucrose by the kg of water in order to get molality.

$$\frac{3.1416\ mol\ \text{Sucrose}}{0.5232\ kg\ \text{Water}} = 6.005\ molal$$

Q.9

A solution contains 75% of ethanol (C_2H_6O) by mass and the rest is water.

a. What is the density of the solution if there is 15 mol of ethanol per liter of solution?
b. To prepare a 3.5L of 2M ethanol, how many milliliters of the solution is needed?

Solution

a) For easy calculation, assume that there is 1 L of the solution. Using:

$$\text{mol} = \text{molarity} \times \text{volume} \tag{11.E.1}$$

The mol of 15M ethanol in 1L is 15 mol. The molar mass of ethanol is $46.068 \frac{g}{mol}$ Using the equation below:

$$\text{ethanol mol} = \frac{\text{mass ethanol}}{\text{ethanol molar mass}} \tag{11.E.2}$$

$$\text{ethanol mass in the solution} = \text{ethanol mol} \times \text{molar mass} = (15 mol)(46.068 \frac{g}{mol}) = 691.02 g \tag{11.E.3}$$

Ethanol is 75% of the solution by mass, therefore:

$$\text{mass of solution} \times 0.75 = \text{mass of ethanol} \tag{11.E.4}$$

$$\text{mass of solution} \times 0.75 = 691.02 g \tag{11.E.5}$$

$$\text{mass of solution} = \frac{691.02 g}{0.75} = 921.36 g \tag{11.E.6}$$

The equation to calculate density is:

$$\text{Density} = \frac{\text{mass}}{\text{volume}} \tag{11.E.7}$$

$$\text{Density} = \frac{921.36 g}{1 L} = 0.921 \frac{g}{ml} \tag{11.E.8}$$

b)To prepare a 3.5L of 2M ethanol;

$$\text{ethanol mol needed} = \text{molarity} \times \text{volume} = (2\,\text{M})(3.5\,\text{L}) = 7\,\text{mol} \tag{11.E.9}$$

$$V_{\text{ethanol needed}} = \frac{\text{mol needed}}{\text{molarity}} = \frac{7\,\text{mol}}{15\,\text{mol}} \times 1\,\text{L} = 0.467\,\text{L} \tag{11.E.10}$$

0.467L of the solution is needed, which is 467mL.

Q.14

Rewrite the following balanced equations as net ionic equations.

a. $H_2SO_4(aq) + 2\,NaOH(aq) \rightarrow 2\,H_2O(l) + Na_2SO_4(aq)$
b. $2\,Na_3PO_4(aq) + 3\,CaCl_2(aq) \rightarrow 6\,NaCl(aq) + Ca_3(PO_4)_2(s)$
c. $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2\,NaCl(aq)$
d. $2\,AgNO_3(aq) + ZnCl_2(aq) \rightarrow 2\,AgCl(s) + Zn(NO_3)_2(aq)$

Solution

a. $2\,H^+(aq) + 2\,OH^-(aq) \longrightarrow 2\,H_2O(l)$
b. $2\,PO_4^{3-}(aq) + 3\,Ca^{2+}(aq) \longrightarrow Ca_3(PO_4)_2(s)$
c. $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$
d. $2\,Ag^{2+}(aq) + Cl^-(aq) \longrightarrow 2\,AgCl(s)$

Q.15

Write the balanced chemical equation for the titration of H_2SO_4 with KOH, then find the volume of a 5.49 M KOH solution needed to neutralize 36.2 g of H_2SO_4 .

Solution

The balanced equation of H_2SO_4 with KOH is:

$$H_2SO_4(aq) + 2\,KOH(aq) \longrightarrow K_2SO_4(aq) + 2\,H_2O(l)$$

Calculate the amount of moles of H_2SO_4 being neutralized:

$$n_{H_2SO_4} = 36.2\text{ g } H_2SO_4 \times \frac{1\text{ mol } H_2SO_4}{98.079\text{ g } H_2SO_4} = 0.369\text{ mol } H_2SO_4$$

Using stoichiometry to find the amount of moles of KOH needed to neutralize the amount of H_2SO_4 present:

$$n_{KOH} = 0.369\text{ mol } H_2SO_4 \times \frac{2\text{ mol KOH}}{1\text{ mol } H_2SO_4} = 0.738\text{ mol KOH}$$

Calculate the volume of the 5.49 M KOH solution needed to neutralize the amount of H_2SO_4 present:

$$V_{KOH} = 0.738\text{ mol KOH} \times \frac{1\text{ L}}{5.49\text{ mol KOH}} = 0.134\text{ L} = 134\text{ mL}$$

Therefore, approximately 134 mL of the 5.49 M KOH solution is needed to neutralize 36.2 g H_2SO_4.

Q.16

Phosphoric acid is made industrially as a by-product of the extraction of calcium phosphate

$$Ca_3(PO_4)_2 + 6\,HNO_3 + 12\,H_2O \longrightarrow 2\,H_3PO_4 + 3\,Ca(NO_3)_2 + 12\,H_2O$$

What volume of 8.5 M phosphoric acid is generated by the reaction of 4.5 metric tons (4500 kg) of calcium phosphate?

Solution

$$4500\text{ kg } Ca_3(PO_4)_2 \times \left(\frac{1000\text{ g}}{1\text{ kg}}\right) \times \left(\frac{1\text{ mol}}{310\text{ g}}\right) \times \left(\frac{2\,H_3PO_4}{1\,Ca_3(PO_4)_2}\right) \times \left(\frac{1\text{ L}}{8.5\text{ moles}}\right) = 3415.56\text{ L } H_3PO_4$$

Q.19

Write a balanced equation for the acid-base reaction that leads to the production of each of the following salts.

a. $BaSO_4$
b. $MgSO_3$
c. $PbSO_4$
d. $AgCl$

Solution

a. $Ba(OH)_2(aq) + H_2SO_4(aq) \rightleftharpoons BaSO_4(s) + 2\,H_2O(l)$
b. $Mg(OH)_2(s) + H_2SO_3(aq) \rightleftharpoons MgSO_3(s) + 2\,H_2O(l)$
c. $Pb(OH)_2(s) + H_2SO_4(aq) \rightleftharpoons PbSO_4(s) + 2\,H_2O(l)$
d. $AgOH(s) + HCl(aq) \rightleftharpoons AgCl(s) + H_2O(l)$

Q.21

Hydrogen selenide is classified as a binary acid that has similar properties as hydrogen sulfide. Write down the balanced equation of hydrogen selenide reacting with the base potassium hydroxide and name the salt product of the reaction.

Solution

https://chem.libretexts.org/@go/page/531549

When the acid H_2S reacts with the base KOH, the reaction goes as follows:

$$H_2S + 2\,KOH \longrightarrow K_2S + 2\,H_2O$$

Forming potassium sulfide.

Similarly, since H_2Se has similar properties as H_2S, a similar reaction occurs:

$$H_2Se + 2\,KOH \longrightarrow K_2Se + 2\,H_2O$$

Potassium selenide is the salt product of the reaction.

Q.25

A student working with an unknown solution of hydrochloric acid is assigned the task of finding its concentration. The student places a 200.0 mL sample of the solution in a 350.0 mL Erlenmeyer flask and titrates the solution with a 0.1234 M solution of sodium hydroxide, where a phenolphthalein indicator is used to find the endpoint. The endpoint is found to be 31.416 mL, what is the concentration of the original hydrochloric acid solution sample?

Solution

Remember that in titration of a strong acid and base, when the endpoint is reached the number of moles used is equal, so the number of moles of NaOH at the endpoint are equal to that of HCl. Use this information to find moles of NaOH from the concentration and volume used to titrate.

$$\text{Concentration of X} = \frac{\text{moles of X}}{\text{liters of X}}$$

Use dimensional analysis to convert concentration of NaOH to moles using the known amount of volume titrated, in liters:

$$0.031416 \cancel{\text{ liter}}\ \text{NaOH} = \frac{0.1234\ \text{mol NaOH}}{1.00\ \cancel{\text{liter}}\ \text{NaOH}} = 0.003877\ \text{mol}$$

Now because we know that the moles of NaOH are equal to the moles of HCl we simply plug in our calculated moles and known original sample volume, in liters, to find the concentration of HCl:

$$\text{Concentration of HCl} = \frac{0.003877\ \text{mol HCl}}{0.200\ \text{liters HCl}} = 0.019385\ \text{M HCl}$$

The concentration of the original hydrochloric acid solution sample was, therefore, 0.019385 M.

Q.41

The vapor pressure of salicylic acid $C_7H_6O_3$ at 200°C is 0.1598 atm. A 19.0 g sample of ethanol C_2H_6O is dissolved in 60.0 g of salicylic acid. Calculate the vapor pressure of salicylic acid above the resulting solution.

Solution

First find the molar masses of salicylic acid and ethanol. Then use them to compute the chemical amounts of the two in solution.

$$n_{C_2H_6O} = 19.0\ g\ C_2H_6O \times \frac{1\ mol\ C_2H_6O}{46.068\ g\ C_2H_6O} = 0.4124\ mol\ C_2H_6O$$

$$n_{C_7H_6O_3} = 60.0\ g\ C_7H_6O_3 \times \frac{1\ mol\ C_7H_6O_3}{138.121\ g\ C_7H_6O_3} = 0.4344\ mol\ C_7H_6O_3$$

The mole fraction of ethanol in the solution equals

$$X_{C_2H_6O} = \frac{0.4124}{0.4344 + 0.4124} = 0.4870$$

The change in vapor pressure of the salicylic acid due to the presence of of the ethanol is

$$\Delta P_{C_4H_6O_3} = -X_{C_4H_6O_3} \times P^{\circ}_{C_4H_6O_3} = -0.5130 \times 0.1518\, atm = -0.08198$$

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

$$\Delta T_b = iK_b m \tag{11.E.11}$$

$$\Delta T_b = 101.1^o\, C - 100^o\, C = 1.1^o\, C \tag{11.E.12}$$

Since the compound was told to not dissociation, we know that the van't Hoff factors is 1:

$$i = 1 \tag{11.E.13}$$

$$m = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{53\, mol}{0.100\, kg} = 0.53 \frac{mol}{g} \tag{11.E.14}$$

$$1.1^oC = (1) \times K_b \times (0.53 \frac{mol}{g}) \tag{11.E.15}$$

$$K_b = \frac{1.1^oC}{0.53 \frac{mol}{kg}} = 2.075 \frac{^oC\, kg}{mol} \tag{11.E.16}$$

This problem does not give the correct constant though 0.513:

https://chem.libretexts.org/Referenc...perties/B5%3A_Ebullioscopic_(Boiling_Point_Elevation)_Constants

Q.45

When 5.82 g of uniformly dissociating unknown salt, YX, is dissolved in 100.0 g of water, the boiling point of the water is raised by 0.20°C. When 7.09 g of uniformly dissociating unknown salt, ZX, is dissolved in 200.0 g of water, the boiling point of the water is raised by 0.30°C. Assuming both have a van't hoff factor of 2, identify the elements that X, Y, and Z represent.

Solution

For both salts, one can utilize the boiling point elevation expression (including the van't hoff factor):

$$\Delta T = i \times K_b \times m$$

and by substituting moles solute over mass solvent into the molality, m, one can derive that:

$$n_{\text{salt}} = \frac{\Delta T \times m_{\text{water}}}{i \times K_b}$$

From this we get the moles of each salt present, and can therefore get their molar mass by dividing their mass by moles present. Next, subtracting the heavier salt by the lighter salt will yield the molar mass of X, $\sim 35.5 \frac{\text{g}}{\text{mol}}$. 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 $451.55\,\mathrm{K}$ and $37.7\frac{\mathrm{K\,kg}}{\mathrm{mol}}$. Find the freezing point of the solution of 0.72 g of glucose is dissolved in the 30.0 g of camphor.

Solution

Since we are evaluating glucose as the solute, $i = 1$.

$$\Delta T = -iK_f m \tag{11.E.17}$$

First find number of moles of glucose in the solution using molar mass.

$$\text{Moles}_{\text{glucose}} = \frac{(0.72g)}{(180.1559\frac{g}{mol})} = 0.0040mol \tag{11.E.18}$$

Molality then can be determined.

$$m = \frac{(0.0040mol)}{(0.030kg)} = 0.13\frac{mol}{kg} \tag{11.E.19}$$

Freezing then can be easily found as such:

$$\Delta T = -iK_f m = -(1)(37.7\frac{^oC\ kg}{mol})(0.13\frac{mol}{kg}) = -4.9^oC \tag{11.E.20}$$

The freezing is $451.55K - 4.9K = 446.65K = 173.5^oC$.

Q.48

It is observed that 2 grams of a non-electrolyte solute dissolved in 100 grams of benzene lowered the freezing point of the solution by 0.40°C compared to pure benzene. Given that the freezing point depression constant of benzene is 5.12 K kg/mol, find the molar mass of the solute. If it is given that the molecular formula of the solute is $\mathrm{X_8}$ where X is an element, what is the formula of the solute?

Solution

$$\Delta T = -ik_f m$$

It is given that

$$\Delta T = 0.40^\circ C \tag{11.E.21}$$

Since the solution is a non-electrolyte, i=1

Hence,

$$\frac{0.40}{K_f} = m$$

$$m = \frac{\frac{2}{\text{Molecular Mass}}}{100 \times 10^{-3}} = \frac{\frac{2}{\text{Molecular Mass}}}{0.1}$$

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

$$27\%\ \text{NaCl(aq)} = \frac{27\ g\ \text{NaCl}}{73\ g\ \text{H}_2\text{O}} \tag{11.E.22}$$

$$molality = \frac{27\ g\ \text{NaCl}}{73\ g\ \text{H}_2\text{O}} \times \frac{mol\ \text{NaCl}}{58.44\ g} \times \frac{1000\ g}{1\ kg} = 6.33\ m \tag{11.E.23}$$

$$\Delta T = -i \times m \times K_p = -2 \times 6.33 \frac{mol}{kg} \times 1.86 \frac{^oC \cdot kg}{mol} = -23.5^oC \tag{11.E.24}$$

The first ice crystal begins to appear at -23.5^oC, as the solution becomes more concentrated, its freezing point decreases further because freezing point depression is a colligative property, so the freezing point of a solution is lower than that of the pure solvent and is directly proportional to the molality of the solute.

Q.50

When homemade ice cream is being made, the temperature ranging downward from -3°C are needed. Ice cubes from a freezer have a temperature of about -12°C, which is cold enough; however, when the ice cream mixture is mixed with the ice cubes, the liquid balances out to 0°C, which is too warm. To obtain a liquid that is cold enough, salt NaCl is dissolved in water and ice is added to the saltwater. The salt lowers the freezing point of the water enough so that it can freeze the liquid inside the ice cream maker. The instruction for the ice cream maker say to add one part salt to 11 parts water (by mass). What is the freezing point of this solution in °C? Assume the NaCl dissociates fully into ions, and that the solution is ideal.

Solution

$$\Delta T_f = -ik_f m \tag{11.E.25}$$

$$\frac{1.00\ g\,\text{NaCl}}{53.5 \frac{g}{mol}} = 0.01869\ mol\ \text{NaCl} \tag{11.E.26}$$

$$m = \frac{0.01869\ mol}{11.00g(\frac{1\ kg}{1000\ g})} = 1.699m \tag{11.E.27}$$

$$x - (-12^\circ C) = -(2) \times (1.86 \frac{^\circ C}{m}) \times (1.699m) \tag{11.E.28}$$

$$x = -18.32^\circ C \tag{11.E.29}$$

Q.53

A sample of a purified unknown compound is dissolved in toluene, diluting the solvent to a volume of 1.05 mL. The resulting solution has an osmotic pressure of 0.025 atm at 275 K. If the solute has a molar mass of 46.06 g/mol, how many grams of the unknown compound were added?

Solution

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

and we know $T = 275K$, $R = 0.0821 \frac{L\ atm}{mol\ K}$ 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^oC 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}:

$$C = 7.8 \times 10^{-4} \frac{M}{atm} \times 4.6\ atm$$
$$C = 0.003588 \frac{mol\ H_2}{L_{\text{water}}}$$

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:

$$C_3H_6 + H_2O \longrightarrow CH_3(CH_2)_2OH$$

- 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 $CH_3(CH_2)_2OH$ 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

$$\Delta H^o_{f(\text{propene})} = 20.4 \frac{kJ}{mol} \tag{11.E.30}$$

$$\Delta H^o_{f(\text{water})} = -241.8 \frac{kJ}{mol} \tag{11.E.31}$$

$$\Delta H^o_{f(\text{CH}_3(\text{CH}_2)_2\text{OH})} = -104.6 \frac{kJ}{mol} \tag{11.E.32}$$

$$\Delta H^o = \Delta H^o_{f(\text{CH}_3(\text{CH}_2)_2\text{OH})} - \Delta H^o_{f(\text{propene})} - \Delta H^o_{f(\text{water})} \tag{11.E.33}$$

$$= -104.6 \frac{kJ}{mol} - (-241.8 \frac{kJ}{mol}) - 20.4 \frac{kJ}{mol} \tag{11.E.34}$$

$$= 116.8 \frac{kJ}{mol} > 0$$

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 $20.0\,^\circ\text{C}$, pure heptane has a vapor pressure of $\text{P}_1{}^\circ = 0.0562\ \text{atm}$ while pure octane has a vapor pressure of $\text{P}_2{}^\circ = 0.0145\ \text{atm}$. What is the mole fraction of heptane vapor over a solution of heptane and octane if the solution contained $0.300\ \text{mol}$ heptane and $0.700\ \text{mol}$ octane?

Solution

Since we have been told to assume the solution is ideal, we can use Raoult's law to obtain the partial pressures of heptane and octane, respectively.

$$P_{\text{heptane}} = \left(\frac{0.300\ \text{mol}}{0.300\ \text{mol} + 0.700\ \text{mol}} \right) \times (0.0562\ \text{atm}) = 0.01686\ \text{atm}$$

$$P_{\text{octane}} = \left(\frac{0.700\ \text{mol}}{0.300\ \text{mol} + 0.700\ \text{mol}} \right) \times (0.0145\ \text{atm}) = 0.01015\ \text{atm}$$

Using the relationship between partial pressure and mole fraction, we can obtain the mole fraction of heptane over the solution. Partial pressure and mole fraction can be related through the ideal gas law $P = n\frac{RT}{V}$. Which shows that under constant temperature and pressure, pressure and number of moles are directly related.

$$\chi_{\text{heptane}} = \left(\frac{0.01686\ \text{atm}}{0.01686\ \text{atm} + 0.01015\ \text{atm}} \right) = 0.624$$

Q.63

At 50ºC, 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 50ºC ?
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 $C_6H_6 = 0.128\ mol$, $X_B =$ the moles of $C_3H_8 = 0.680\ mol$,

$$\chi_B = \frac{0.0929\ kPa}{6.81\ kPa} = 0.0136$$

Plug into the equation and solve:

$$\left(\frac{0.128\ mol}{0.128 + 0.680\ mol}\right) = 0.158$$

b) Since the problem states that the result of mixing the two solutions is nearly ideal, we can assume an ideal solution is formed and use Raoult's Law and we can choose to keep pressure in units of kPa OR torr.

lt'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 $CaCl_2(s)$, 2g of $MgCl_2(s)$, and 3g of $MnO_2(s)$ in enough water to make a total volume of 150 mL. Calculate the concentration of chlorine in the solution in grams per liter.

Solution

$m_{Cl} = 2g\,CaCl_2(\frac{2(35.5g\,Cl)}{110.98g\,CaCl_2}) + 2g\,MgCl_2(\frac{2(35.5g\,Cl)}{95.12g\,MgCl_2})$

$m_{Cl} = 2.77g\,Cl$

mass of chlorine per liter: $\frac{2.77g\,Cl}{150\times10^{-3}L} = 18.5\,\frac{g}{L}$

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 = $M \times V$

$= 0.1 \times 10\text{ mL} = 1\text{ mmol} = 10^{-3}$ moles

Since only one mole of X was used for every mole of Chromium Hydroxide, the number of moles reacted are equal.

$\frac{\text{Mass}}{\text{Molar mass}}$ = number of moles, hence for X,

$\frac{0.05\text{ g}}{(0.01\text{L}\times0.1\text{M})} = 50\,\frac{\text{g}}{\text{mol}}$

(b) $\frac{0.05\text{ g}}{(0.01\text{L}\times0.1\text{M}\times5)} = 10\,\frac{\text{g}}{\text{mol}}$

Q.71

A 0.200 g sample of chloride with unknown purity was dissolved in 200 mL of water was then titrated with $AgNO_3$ 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:

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

Next we need to determine the amount of moles of Ag used during the titration:

$$\text{mol } Ag^+ = 28\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.1\text{ mol}}{1\ \cancel{L}}\right) = 2.80\times10^{-3}\text{ mol } Ag^+$$

Now that we know the amount of moles of Ag reacted because Ag and Cl combine at a one to one ration we can find the mass of Cl used:

$$\text{mass } Cl^- = 2.80\times10^{-3}\ \cancel{mol}\left(\frac{35.45\text{ g}}{1\ \cancel{mol}}\right) = 9.92\times10^{-2}\text{ g } Cl^-$$

Now that we know the mass of Cl in the unknown we can calculate the mass percent:

$$100\%\left(\frac{0.0992\text{ g}}{0.2\text{g}}\right) = 49.63\%$$

Q.73

At 20°C, the vapor pressure of pure water is 17.5 mmHg. When 110 g of a substance X_y is dissolved in 500 g of water, the vapor pressure of the solution is 15.0 mmHg. Given that this substance has a molecular mass of 12.011 g/mol, what is the molecular formula of this substance X_y. (i.e. what is the number value of subscript y).

Solution

For this question, we can use Raoult's Law

$$P_{\text{solution}} = \chi_{\text{solvent}} \times P^\circ{}_{\text{solvent}}$$

First, we plug in the known values of the pressure of the solution and the pressure of the pure solvent, water, to find the mole fraction.

$$15.0 \text{ mmHg} = \chi_{\text{solvent}} \times 17.5 \text{ mmHg}$$

$$\chi_{\text{solvent}} = 0.8571$$

Next, we can calculate the the number of moles of the solvent from its mass and molecular weight.

$$\text{Moles of solvent} = 500 \text{ g} \times \frac{1}{18.015 \text{ g/mol}} = 27.75 \text{ moles}$$

Next, we can calculate the moles of the solute from the mole fraction of the solvent

$$0.8571 = \frac{27.75 \text{ moles}}{27.75 \text{ moles } + \text{ moles of } X_y}$$

$$\text{moles of } X_y = 4.63 \text{ moles}$$

From here, we can calculate the molecular formula of the substance by dividing the amount of grams per mole used in the solution by the molecular mass of the substance.

$$\frac{110 \text{ g}}{4.63 \text{ moles}} = 23.76 \text{ g/mol}$$

$$(23.76 \text{ g/mol}) \times (\frac{1}{12.011 \text{ g/mol}}) = 1.98$$

$$1.98 \approx 2$$

Thus, the molecular formula of our substance is X_2.

Q.81

The cell membrane of a plant cell is permeable to water. In a salt solution, the plant cells shrivel (lose water) when the concentration is high, and swell (take up water) when the concentration is low. Scientists perform an experiment at 30°C, where an aqueous solution of NaCl with a freezing point of -0.028°C is used to water the plant cells. This causes the plant cells to neither swell nor shrink indicating that the osmotic pressure of the plant cell contents is equal to that of the NaCl solution. Assuming the molarity and molality of the plant cell contents are equal, calculate the osmotic pressure of the solution inside the plant cells. The K_f for the solution is $1.86 \frac{\text{K kg}}{\text{mol}}$.

Solution

Plug in the given values into the equation for freezing point depression to solve for the molality of the solution

$$\Delta T_f = -K_f m$$

$$-0.0218 = -1.86 K \cdot kg \cdot mol^{-1} m$$

$$m = 0.015 \frac{kg}{mol}$$

Because the plant cell neither swells nor shrinks, the molality of the solution is equivalent to the molality of the plant cell contents. According to the question, assume the molarity and molality are equal so concentration

$$c = 0.15 M$$

Use the following equation to calculate for the osmotic pressure, π.

$$\pi = cRT$$
$$= (0.15M)(0.08206\frac{L\,atm}{mol\,K})(303.15K)$$
$$= 0.374atm$$

Q.83

Jim loves the smell of grass. He loves it so much that he frequently sniffs the fumes from 1-Hexanol, which is a chemical compound that is known to smell like grass trimmings. Because of his love, he decides to make his garage into a “gas den”, and aimed to have 60% of the air in it as 1-Hexanol gas. He achieves this by filling a pool with a mixture of 1-Hexanol and Water. Assume that the air in the “gas den” consists of only the fumes from this mixture. If the pool has 10000L of water in it, how many litres of 1-Hexanol does he need? Use Henry’s Law to determine this amount.

Relevant Information:

1-Hexanol:

- Density: $814\frac{kg}{m^3}$
- Molar mass: $107.1748\frac{g}{mol}$
- Henry’s Law Constant: $64\frac{molal}{bar}$

Water:

- Density: $1000\frac{kg}{m^3}$

Solution

This problem asks for the amount, in litres, of 1-Hexanol that is required to make Jim’s dreams come true. The information given is the density of 1-Hexanol and its molar mass, but since they don’t have very much to do with pressure, they can be set aside for now. The question explicitly mentions that Henry’s Law should be used, so start be identifying what Henry’s Law actually does:

$$C = kP$$

Where C is concentration, k is Henry’s Law constant, and P is partial pressure. The question gives out the fact that Jim wants the air in his garage to be 60% 1-Hexanol vapor. Remember the total pressure of air is 1 atm ≈ 1 bar (ignore the error here). Therefore, the partial pressure of 1-hexanol is $1\text{ bar} \times 60\% = 0.6\text{ bar}$. The Henry’s Law constant is also provided, and by plugging those two in, the concentration of 1-Hexanol in the desired “solution” (more accurately, giant pool of chemicals) is found. This process is shown below:

$$C = kP = (64\frac{molal}{bar}) \times 0.6\text{ bar} = 38.4$$

This concentration, from the units of k, is in mo*lality*, which is $\frac{mol_{\text{solute}}}{kg_{\text{solvent}}}$. Now all that is left is to convert molality to litres. By utilizing the molar mass of 1-Hexanol:

$$38.4\frac{mol_{\text{solute}}}{kg_{\text{solvent}}} \times 107.1748\frac{g}{mol} \approx 4115.51\frac{g_{\text{solute}}}{kg_{\text{solvent}}}$$

We know that the solvent is water, and that water has a density of $1000\frac{kg}{m^3}$. Also, the conversion rate of m^3 to L is 1:1000. Therefore, the equation can be solved as follows.

$$4115.51\frac{g_{\text{solute}}}{kg_{\text{solvent}}} \times 1000\frac{kg_{H_2O}}{m^3} \times \frac{m^3}{1000\,L_{H_2O}} \approx 4115.51\frac{g_{\text{solute}}}{L_{\text{solvent}}}$$

We now have the value for how many grams of solute (1-Hexanol) there should be per litre of solvent. simply divide this value by the density to obtain litres of 1-Hexanol per litre of water. Multiply this number by the amount of water in the pool to get the desired amount of solute that is needed for the solution! (note that the density was converted to $\frac{g}{L}$,

$$4115.51\frac{g_{\text{solute}}}{L_{\text{solvent}}} \div \left(814000\frac{g_{\text{1-hexanol}}}{L}\right) \times 10000 L_{\text{H}_2\text{O}} = 50.56\,\text{L}$$

~~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 $78.5\,\frac{\text{g}}{\text{mol}}$. Find the molecular formula of this sample.

Solution

First, the moles of each Nitrogen, Hydrogen, and Oxygen in solution are calculated:

$$mol_N = 4g\,\text{NO}_2 \times \left(\frac{1\ mol\ \text{NO}_2}{46.005\frac{g}{mol}}\right) \times \left(\frac{1\ mol\ N}{1\ mol\ \text{NO}_2}\right) = 0.0869\ mol$$

$$mass_N = \left(14.00\frac{g}{mol}\right)(0.0869 mol) = 1.2172g\,\text{N}$$

$$mol_H = 7g\,\text{H}_2\text{O} \times \left(\frac{1\ mol\ H_2O}{18.02\frac{g}{mol}}\right) \times \left(\frac{2\ mol\ H}{1\ mol\ \text{H}_2\text{O}}\right) = 0.7769\ mol$$

$$mass_H = \left(1.01\frac{g}{mol}\right)(0.7769 mol) = 0.7847g\,\text{H}$$

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 $\text{H}_{0.7769}\text{N}_{0.0869}\text{O}_{0.0936}$, creating an empirical formula H_9NO

From here, the molecular formula can be established using the molar mass:

$$\text{Empirical formula mass} = 9\left(1.01\frac{g}{mol\ H}\right) + \left(14.00\frac{g}{mol\ N}\right) + \left(15.9994\frac{g}{mol\ O}\right)$$

$$\text{Empirical formula mass} = 39.0894\frac{g}{mol}$$

$$\text{Sample Mass} = 78.5\frac{g}{mol}$$

$$\frac{78.5\frac{g}{mol}}{39.084\frac{g}{mol}} = 2.00$$

$$2(\text{H}_9\text{NO}) = \text{H}_{18}\text{N}_2\text{O}_2 = \text{Molecular Formula}$$

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

$$C_xH_yO_z + O_2 \longrightarrow H_2O + CO_2$$

The molar masses of carbon, hydrogen, and oxygen are 12.01 g/mol, 1.008 g/mol, and 16.00 g/mol respectively. Therefore the molar masses of water and carbon dioxide are $18.016 \frac{g}{mol}$ and $44.01 \frac{g}{mol}$ These values can be used to determine the mass percent of hydrogen in water

$$\frac{2(1.008)\ \frac{g}{mol}}{18.016\ \frac{g}{mol}} \times 100 = 11.2\%$$

And the mass percent of carbon in carbon dioxide

$$\frac{12.01\ \frac{g}{mol}}{44.01\ \frac{g}{mol}} \times 100 = 27.3\%$$

The mass percents can be used to determine the amount of hydrogen and carbon are present.

$$3.00\ g \times 0.112 = 0.336\ g \text{ of Hydrogen}$$

$$7.33\ g \times 0.273 = 2.001\ g \text{ of Carbon}$$

By subtracting the masses of Carbon and Hydrogen from the original mass of the substance, the mass of oxygen present in the substance can be found

$$5\ g - (0.336\ g + 2.001\ g) = 2.663\ g \text{ of Oxygen}$$

By dividing the masses present by the molar mass, the amount of moles of each element can be determined

$$\frac{0.112\ g}{1.008\ \frac{g}{mol}} = 0.333\ mol \text{ of Hydrogen}$$

$$\frac{2.001\ g}{12.01\ \frac{g}{mol}} = 0.167\ mol \text{ of Carbon}$$

$$\frac{2.663\ g}{16.00\ \frac{g}{mol}} = 0.166\ mol \text{ of Oxygen}$$

By looking at the amount of moles of each element, it can be noticed that there are equal amounts of carbon and oxygen and twice as much hydrogen as carbon or oxygen. Therefore the ratio of $C : H : O$ in the substance is $1 : 2 : 1$. However, the molar mass of the substance remains unknown, but it can be found using the information about the freezing point depression.

From the formula for freezing point depression

$$\Delta T = -i \times k_f \times m$$

$$-0.0605^\circ C = -1 \times 0.512^\circ C\ m^{-1} \times m$$

$$m = \frac{0.0605^\circ C}{0.512 \frac{^\circ C}{m}} = 0.118\ \frac{mol}{kg}$$

By multiply by the mass of solvent (water), we can determine the amount of moles that was dissolved in the water

$$0.118\ \frac{mol}{kg} \times 0.5\ kg = 0.059\ mol$$

The last step in finding the molar mass of the substance is to divide the mass dissolved by the moles dissolved

$$\frac{10.64\ g}{0.059\ mol} = 180.3\ \frac{g}{mol}$$

Now we can find the formula of the substance. The first step is to find the number of moles of the substance combusted

$$\frac{5\ g}{180.3\ \frac{g}{mol}} = 0.0277\ mol$$

We can compare this to the number of carbon moles combusted to determine the number of carbon atoms per molecule of the substance

$$\frac{0.167\ g\ \text{of Carbon}}{0.0277\ mol} = 6\ \text{Carbon atoms}$$

When we apply the number of carbon atoms to the ratio of elements found earlier, the chemical formula comes to be $C_6H_{12}O_6$ which is glucose.

Answer: Glucose

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CHAPTER OVERVIEW

12: Kinetics

Chemical kinetics is the study of rates of chemical processes and includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

12.1: Introduction
12.2: Summary
12.3: Exercises
12.4: Chemical Reaction Rates
12.5: Factors Affecting Reaction Rates
12.6: Rate Laws
12.7: Integrated Rate Laws
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12.10: Catalysis
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12.12: Key Equations

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12.1: Introduction

The lizard in the photograph is not simply enjoying the sunshine or working on its tan. The heat from the sun's rays is critical to the lizard's survival. A warm lizard can move faster than a cold one because the chemical reactions that allow its muscles to move occur more rapidly at higher temperatures. A cold lizard is a slower lizard and an easier meal for predators.



Figure 12.1.1: An agama lizard basks in the sun. As its body warms, the chemical reactions of its metabolism speed up.

From baking a cake to determining the useful lifespan of a bridge, rates of chemical reactions play important roles in our understanding of processes that involve chemical changes. Two questions are typically posed when planning to carry out a chemical reaction. The first is: "Will the reaction produce the desired products in useful quantities?" The second question is: "How rapidly will the reaction occur?" A third question is often asked when investigating reactions in greater detail: "What specific molecular-level processes take place as the reaction occurs?" Knowing the answer to this question is of practical importance when the yield or rate of a reaction needs to be controlled.

The study of chemical kinetics concerns the second and third questions—that is, the rate at which a reaction yields products and the molecular-scale means by which a reaction occurs. This chapter examines the factors that influence the rates of chemical reactions, the mechanisms by which reactions proceed, and the quantitative techniques used to describe the rates at which reactions occur.

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12.2: Summary

The rate of a reaction can be expressed either in terms of the decrease in the amount of a reactant or the increase in the amount of a product per unit time. Relations between different rate expressions for a given reaction are derived directly from the stoichiometric coefficients of the equation representing the reaction.

The rate of a chemical reaction is affected by several parameters. Reactions involving two phases proceed more rapidly when there is greater surface area contact. If temperature or reactant concentration is increased, the rate of a given reaction generally increases as well. A catalyst can increase the rate of a reaction by providing an alternative pathway with a lower activation energy.

Rate laws (*differential rate laws*) provide a mathematical description of how changes in the concentration of a substance affect the rate of a chemical reaction. Rate laws are determined experimentally and cannot be predicted by reaction stoichiometry. The order of reaction describes how much a change in the concentration of each substance affects the overall rate, and the overall order of a reaction is the sum of the orders for each substance present in the reaction. Reaction orders are typically first order, second order, or zero order, but fractional and even negative orders are possible.

Integrated rate laws are mathematically derived from differential rate laws, and they describe the time dependence of reactant and product concentrations.

The half-life of a reaction is the time required to decrease the amount of a given reactant by one-half. A reaction's half-life varies with rate constant and, for some reaction orders, reactant concentration. The half-life of a zero-order reaction decreases as the initial concentration of the reactant in the reaction decreases. The half-life of a first-order reaction is independent of concentration, and the half-life of a second-order reaction decreases as the concentration increases.

Chemical reactions typically require collisions between reactant species. These reactant collisions must be of proper orientation and sufficient energy in order to result in product formation. Collision theory provides a simple but effective explanation for the effect of many experimental parameters on reaction rates. The Arrhenius equation describes the relation between a reaction's rate constant, activation energy, temperature, and dependence on collision orientation.

The sequence of individual steps, or elementary reactions, by which reactants are converted into products during the course of a reaction is called the reaction mechanism. The molecularity of an elementary reaction is the number of reactant species involved, typically one (unimolecular), two (bimolecular), or, less commonly, three (termolecular). The overall rate of a reaction is determined by the rate of the slowest in its mechanism, called the rate-determining step. Unimolecular elementary reactions have first-order rate laws, while bimolecular elementary reactions have second-order rate laws. By comparing the rate laws derived from a reaction mechanism to that determined experimentally, the mechanism may be deemed either incorrect or plausible.

Catalysts affect the rate of a chemical reaction by altering its mechanism to provide a lower activation energy. Catalysts can be homogenous (in the same phase as the reactants) or heterogeneous (a different phase than the reactants).

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12.3: Exercises

1.

What is the difference between average rate, initial rate, and instantaneous rate?

2.

Ozone decomposes to oxygen according to the equation Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.

3.

In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction Write the equation that relates the rate expressions for this reaction in terms of the disappearance of Cl_2 and F_2 and the formation of ClF_3.

4.

A study of the rate of dimerization of C_4H_6 gave the data shown in the table:

Time (s)	0	1600	3200	4800	6200
$[C_4H_6]$ (M)	$1.00\ 10^{-2}$	$5.04\ 10^{-3}$	$3.37\ 10^{-3}$	$2.53\ 10^{-3}$	$2.08\ 10^{-3}$

a. Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.
b. Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus $[C_4H_6]$. What are the units of this rate?
c. Determine the average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s from the rates found in parts (a) and (b).

5.

A study of the rate of the reaction represented as gave the following data:

Time (s)	0.0	5.0	10.0	15.0	20.0	25.0	35.0
[A] (M)	1.00	0.775	0.625	0.465	0.360	0.285	0.230

a. Determine the average rate of disappearance of A between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.
b. Estimate the instantaneous rate of disappearance of A at 15.0 s from a graph of time versus [A]. What are the units of this rate?
c. Use the rates found in parts (a) and (b) to determine the average rate of formation of B between 0.00 s and 10.0 s, and the instantaneous rate of formation of B at 15.0 s.

6.

Consider the following reaction in aqueous solution:

If the rate of disappearance of $Br^-(aq)$ at a particular moment during the reaction is $3.5\ 10^{-4}$ mol L^{-1} s^{-1}, what is the rate of appearance of $Br_2(aq)$ at that moment?

7.

Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

8.

Explain why an egg cooks more slowly in boiling water in Denver than in New York City. (Hint: Consider the effect of temperature on reaction rate and the effect of pressure on boiling point.)

9.

Go to the PhET Reactions & Rates interactive. Use the Single Collision tab to represent how the collision between monatomic oxygen (O) and carbon monoxide (CO) results in the breaking of one bond and the formation of another. Pull back on the red plunger to release the atom and observe the results. Then, click on “Reload Launcher” and change to “Angled shot” to see the difference.

a. What happens when the angle of the collision is changed?
b. Explain how this is relevant to rate of reaction.

10.

In the PhET Reactions & Rates interactive, use the “Many Collisions” tab to observe how multiple atoms and molecules interact under varying conditions. Select a molecule to pump into the chamber. Set the initial temperature and select the current amounts of each reactant. Select “Show bonds” under Options. How is the rate of the reaction affected by concentration and temperature?

11.

In the PhET Reactions & Rates interactive, on the Many Collisions tab, set up a simulation with 15 molecules of A and 10 molecules of BC. Select “Show Bonds” under Options.

a. Leave the Initial Temperature at the default setting. Observe the reaction. Is the rate of reaction fast or slow?
b. Click “Pause” and then “Reset All,” and then enter 15 molecules of A and 10 molecules of BC once again. Select “Show Bonds” under Options. This time, increase the initial temperature until, on the graph, the total average energy line is completely above the potential energy curve. Describe what happens to the reaction.

12.

How do the rate of a reaction and its rate constant differ?

13.

Doubling the concentration of a reactant increases the rate of a reaction four times. With this knowledge, answer the following questions:

a. What is the order of the reaction with respect to that reactant?
b. Tripling the concentration of a different reactant increases the rate of a reaction three times. What is the order of the reaction with respect to that reactant?

14.

Tripling the concentration of a reactant increases the rate of a reaction nine-fold. With this knowledge, answer the following questions:

a. What is the order of the reaction with respect to that reactant?
b. Increasing the concentration of a reactant by a factor of four increases the rate of a reaction four-fold. What is the order of the reaction with respect to that reactant?

15.

How will the rate of reaction change for the process: if the rate law for the reaction is

a. Decreasing the pressure of NO_2 from 0.50 atm to 0.250 atm.
b. Increasing the concentration of CO from 0.01 *M* to 0.03 *M*.

16.

How will each of the following affect the rate of the reaction: if the rate law for the reaction is ?

a. Increasing the pressure of NO_2 from 0.1 atm to 0.3 atm
b. Increasing the concentration of CO from 0.02 *M* to 0.06 *M*.

17.

Regular flights of supersonic aircraft in the stratosphere are of concern because such aircraft produce nitric oxide, NO, as a byproduct in the exhaust of their engines. Nitric oxide reacts with ozone, and it has been suggested that this could contribute to depletion of the ozone layer. The reaction is first order with respect to both NO and O_3 with a rate constant of $2.20\ 10^7$ L/mol/s. What is the instantaneous rate of disappearance of NO when $[NO] = 3.3\ 10^{-6}$ *M* and $[O_3] = 5.9\ 10^{-7}$ *M*?

18.

Radioactive phosphorus is used in the study of biochemical reaction mechanisms because phosphorus atoms are components of many biochemical molecules. The location of the phosphorus (and the location of the molecule it is bound in) can be detected from the electrons (beta particles) it produces:

rate = $4.85\ 10^{-2}$

What is the instantaneous rate of production of electrons in a sample with a phosphorus concentration of 0.0033 *M*?

19.

The rate constant for the radioactive decay of ^{14}C is $1.21\ 10^{-4}$ $year^{-1}$. The products of the decay are nitrogen atoms and electrons (beta particles):

What is the instantaneous rate of production of N atoms in a sample with a carbon-14 content of $6.5\ 10^{-9}$ *M*?

20.

The decomposition of acetaldehyde is a second order reaction with a rate constant of $4.71\ 10^{-8}$ L mol^{-1} s^{-1}. What is the instantaneous rate of decomposition of acetaldehyde in a solution with a concentration of $5.55\ 10^{-4}$ *M*?

21.

Alcohol is removed from the bloodstream by a series of metabolic reactions. The first reaction produces acetaldehyde; then other products are formed. The following data have been determined for the rate at which alcohol is removed from the blood of an average male, although individual rates can vary by 25–30%. Women metabolize alcohol a little more slowly than men:

$[C_2H_5OH]$ (*M*)	$4.4\ 10^{-2}$	$3.3\ 10^{-2}$	$2.2\ 10^{-2}$
Rate (mol L^{-1} h^{-1})	$2.0\ 10^{-2}$	$2.0\ 10^{-2}$	$2.0\ 10^{-2}$

Determine the rate law, the rate constant, and the overall order for this reaction.

22.

Under certain conditions the decomposition of ammonia on a metal surface gives the following data:

$[NH_3]$ (*M*)	$1.0\ 10^{-3}$	$2.0\ 10^{-3}$	$3.0\ 10^{-3}$
Rate (mol L^{-1} h^{-1})	$1.5\ 10^{-6}$	$1.5\ 10^{-6}$	$1.5\ 10^{-6}$

Determine the rate law, the rate constant, and the overall order for this reaction.

23.

Nitrosyl chloride, NOCl, decomposes to NO and Cl_2.

Determine the rate law, the rate constant, and the overall order for this reaction from the following data:

[NOCl] (*M*)	0.10	0.20	0.30
Rate (mol L^{-1} h^{-1})	$8.0\ 10^{-10}$	$3.2\ 10^{-9}$	$7.2\ 10^{-9}$

24.

From the following data, determine the rate law, the rate constant, and the order with respect to *A* for the reaction

[*A*] (*M*)	$1.33\ 10^{-2}$	$2.66\ 10^{-2}$	$3.99\ 10^{-2}$
Rate (mol L^{-1} h^{-1})	$3.80\ 10^{-7}$	$1.52\ 10^{-6}$	$3.42\ 10^{-6}$

25.

Nitrogen monoxide reacts with chlorine according to the equation:

The following initial rates of reaction have been observed for certain reactant concentrations:

[NO] (mol/L)	$[Cl_2]$ (mol/L)	Rate (mol L^{-1} h^{-1})

[NO] (mol/L)	$[Cl_2]$ (mol/L)	Rate (mol L^{-1} h^{-1})
0.50	0.50	1.14
1.00	0.50	4.56
1.00	1.00	9.12

What is the rate law that describes the rate's dependence on the concentrations of NO and Cl_2? What is the rate constant? What are the orders with respect to each reactant?

26.

Hydrogen reacts with nitrogen monoxide to form dinitrogen monoxide (laughing gas) according to the equation:

Determine the rate law, the rate constant, and the orders with respect to each reactant from the following data:

[NO] (*M*)	0.30	0.60	0.60
$[H_2]$ (*M*)	0.35	0.35	0.70
Rate (mol L^{-1} s^{-1})	$2.835\ 10^{-3}$	$1.134\ 10^{-2}$	$2.268\ 10^{-2}$

27.

For the reaction the following data were obtained at 30 °C:

[*A*] (*M*)	0.230	0.356	0.557
Rate (mol L^{-1} s^{-1})	$4.17\ 10^{-4}$	$9.99\ 10^{-4}$	$2.44\ 10^{-3}$

a. What is the order of the reaction with respect to [*A*], and what is the rate law?
b. What is the rate constant?

28.

For the reaction the following data were obtained at 30 °C:

$[Q]_{initial}$ (*M*)	0.170	0.212	0.357
Rate (mol L^{-1} s^{-1})	$6.68\ 10^{-3}$	$1.04\ 10^{-2}$	$2.94\ 10^{-2}$

a. What is the order of the reaction with respect to [*Q*], and what is the rate law?
b. What is the rate constant?

29.

The rate constant for the first-order decomposition at 45 °C of dinitrogen pentoxide, N_2O_5, dissolved in chloroform, $CHCl_3$, is $6.2\ 10^{-4}$ min^{-1}.

What is the rate of the reaction when $[N_2O_5] = 0.40$ *M*?

30.

The annual production of HNO_3 in 2013 was 60 million metric tons Most of that was prepared by the following sequence of reactions, each run in a separate reaction vessel.

a. The first reaction is run by burning ammonia in air over a platinum catalyst. This reaction is fast. The reaction in equation (c) is also fast. The second reaction limits the rate at which nitric acid can be prepared from ammonia. If equation (b) is second order in NO and first order in O_2, what is the rate of formation of NO_2 when the oxygen concentration is 0.50 *M* and the nitric oxide concentration is 0.75 *M*? The rate constant for the reaction is $5.8\ 10^{-6}$ L^2 mol^{-2} s^{-1}.

31.

The following data have been determined for the reaction:

	1	2	3
(M)	0.10	0.20	0.30
(M)	0.050	0.050	0.010
Rate (mol L^{-1} s^{-1})	$3.05\ 10^{-4}$	$6.20\ 10^{-4}$	$1.83\ 10^{-4}$

Determine the rate law and the rate constant for this reaction.

32.

Describe how graphical methods can be used to determine the order of a reaction and its rate constant from a series of data that includes the concentration of A at varying times.

33.

Use the data provided to graphically determine the order and rate constant of the following reaction:

Time (s)	0	$5.00\ 10^3$	$1.00\ 10^4$	$1.50\ 10^4$
$[SO_2Cl_2]$ (M)	0.100	0.0896	0.0802	0.0719
Time (s)	$2.50\ 10^4$	$3.00\ 10^4$	$4.00\ 10^4$	
$[SO_2Cl_2]$ (M)	0.0577	0.0517	0.0415	

34.

Pure ozone decomposes slowly to oxygen, Use the data provided in a graphical method and determine the order and rate constant of the reaction.

Time (h)	0	$2.0\ 10^3$	$7.6\ 10^3$	$1.00\ 10^4$
$[O_3]$ (M)	$1.00\ 10^{-5}$	$4.98\ 10^{-6}$	$2.07\ 10^{-6}$	$1.66\ 10^{-6}$
Time (h)	$1.23\ 10^4$	$1.43\ 10^4$	$1.70\ 10^4$	
$[O_3]$ (M)	$1.39\ 10^{-6}$	$1.22\ 10^{-6}$	$1.05\ 10^{-6}$	

35.

From the given data, use a graphical method to determine the order and rate constant of the following reaction:

Time (s)	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
[X] (M)	0.0990	0.0497	0.0332	0.0249	0.0200	0.0166	0.0143	0.0125

36.

What is the half-life for the first-order decay of phosphorus-32? The rate constant for the decay is $4.85\ 10^{-2}$ day^{-1}.

37.

What is the half-life for the first-order decay of carbon-14? The rate constant for the decay is $1.21\ 10^{-4}$ $year^{-1}$.

38.

What is the half-life for the decomposition of NOCl when the concentration of NOCl is 0.15 M? The rate constant for this second-order reaction is $8.0\ 10^{-8}$ L mol^{-1} s^{-1}.

39.

What is the half-life for the decomposition of O_3 when the concentration of O_3 is $2.35\ 10^{-6}$ M? The rate constant for this second-order reaction is 50.4 L mol^{-1} h^{-1}.

40.

The reaction of compound *A* to give compounds *C* and *D* was found to be second-order in *A*. The rate constant for the reaction was determined to be 2.42 L mol^{-1} s^{-1}. If the initial concentration is 0.500 mol/L, what is the value of $t_{1/2}$?

41.

The half-life of a reaction of compound *A* to give compounds *D* and *E* is 8.50 min when the initial concentration of *A* is 0.150 M. How long will it take for the concentration to drop to 0.0300 M if the reaction is (a) first order with respect to *A* or (b) second order with respect to *A*?

42.

Some bacteria are resistant to the antibiotic penicillin because they produce penicillinase, an enzyme with a molecular weight of 3 10^4 g/mol that converts penicillin into inactive molecules. Although the kinetics of enzyme-catalyzed reactions can be complex, at low concentrations this reaction can be described by a rate law that is first order in the catalyst (penicillinase) and that also involves the concentration of penicillin. From the following data: 1.0 L of a solution containing 0.15 µg (0.15 10^{-6} g) of penicillinase, determine the order of the reaction with respect to penicillin and the value of the rate constant.

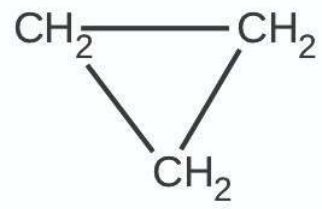
[Penicillin] (*M*)	Rate (mol L^{-1} min^{-1})
2.0 10^{-6}	1.0 10^{-10}
3.0 10^{-6}	1.5 10^{-10}
4.0 10^{-6}	2.0 10^{-10}

43.

Both technetium-99 and thallium-201 are used to image heart muscle in patients with suspected heart problems. The half-lives are 6 h and 73 h, respectively. What percent of the radioactivity would remain for each of the isotopes after 2 days (48 h)?

44.

There are two molecules with the formula C_3H_6. Propene, is the monomer of the polymer polypropylene, which is used for indoor-outdoor carpets. Cyclopropane is used as an anesthetic:



When heated to 499 °C, cyclopropane rearranges (isomerizes) and forms propene with a rate constant of 5.95 10^{-4} s^{-1}. What is the half-life of this reaction? What fraction of the cyclopropane remains after 0.75 h at 499 °C?

45.

Fluorine-18 is a radioactive isotope that decays by positron emission to form oxygen-18 with a half-life of 109.7 min. (A positron is a particle with the mass of an electron and a single unit of positive charge; the equation is Physicians use ^{18}F to study the brain by injecting a quantity of fluoro-substituted glucose into the blood of a patient. The glucose accumulates in the regions where the brain is active and needs nourishment.

a. What is the rate constant for the decomposition of fluorine-18?
b. If a sample of glucose containing radioactive fluorine-18 is injected into the blood, what percent of the radioactivity will remain after 5.59 h?
c. How long does it take for 99.99% of the ^{18}F to decay?

46.

Suppose that the half-life of steroids taken by an athlete is 42 days. Assuming that the steroids biodegrade by a first-order process, how long would it take for of the initial dose to remain in the athlete's body?

47.

Recently, the skeleton of King Richard III was found under a parking lot in England. If tissue samples from the skeleton contain about 93.79% of the carbon-14 expected in living tissue, what year did King Richard III die? The half-life for carbon-14 is 5730 years.

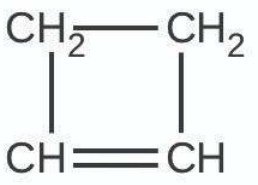
48.

Nitroglycerine is an extremely sensitive explosive. In a series of carefully controlled experiments, samples of the explosive were heated to 160 °C and their first-order decomposition studied. Determine the average rate constants for each experiment using the following data:

Initial $[C_3H_5N_3O_9]$ (M)	4.88	3.52	2.29	1.81	5.33	4.05	2.95	1.72
t (s)	300	300	300	300	180	180	180	180
% Decomposed	52.0	52.9	53.2	53.9	34.6	35.9	36.0	35.4

49.

For the past 10 years, the unsaturated hydrocarbon 1,3-butadiene has ranked 38th among the top 50 industrial chemicals. It is used primarily for the manufacture of synthetic rubber. An isomer exists also as cyclobutene:



The isomerization of cyclobutene to butadiene is first-order and the rate constant has been measured as 2.0 10^{-4} s^{-1} at 150 °C in a 0.53-L flask. Determine the partial pressure of cyclobutene and its concentration after 30.0 minutes if an isomerization reaction is carried out at 150 °C with an initial pressure of 55 torr.

50.

Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

51.

When every collision between reactants leads to a reaction, what determines the rate at which the reaction occurs?

52.

What is the activation energy of a reaction, and how is this energy related to the activated complex of the reaction?

53.

Account for the relationship between the rate of a reaction and its activation energy.

54.

Describe how graphical methods can be used to determine the activation energy of a reaction from a series of data that includes the rate of reaction at varying temperatures.

55.

How does an increase in temperature affect rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.

56.

The rate of a certain reaction doubles for every 10 °C rise in temperature.

a. How much faster does the reaction proceed at 45 °C than at 25 °C?

b. How much faster does the reaction proceed at 95 °C than at 25 °C?

57.

In an experiment, a sample of $NaClO_3$ was 90% decomposed in 48 min. Approximately how long would this decomposition have taken if the sample had been heated 20 °C higher? (Hint: Assume the rate doubles for each 10 °C rise in temperature.)

58.

The rate constant at 325 °C for the decomposition reaction is 6.1 10^{-8} s^{-1}, and the activation energy is 261 kJ per mole of C_4H_8. Determine the frequency factor for the reaction.

59.

The rate constant for the decomposition of acetaldehyde, CH_3CHO, to methane, CH_4, and carbon monoxide, CO, in the gas phase is 1.1 10^{-2} L mol^{-1} s^{-1} at 703 K and 4.95 L mol^{-1} s^{-1} at 865 K. Determine the activation energy for this decomposition.

60.

An elevated level of the enzyme alkaline phosphatase (ALP) in human serum is an indication of possible liver or bone disorder. The level of serum ALP is so low that it is very difficult to measure directly. However, ALP catalyzes a number of reactions, and its relative concentration can be determined by measuring the rate of one of these reactions under controlled conditions. One such reaction is the conversion of p-nitrophenyl phosphate (PNPP) to p-nitrophenoxide ion (PNP) and phosphate ion. Control of temperature during the test is very important; the rate of the reaction increases 1.47 times if the temperature changes from 30 °C to 37 °C. What is the activation energy for the ALP–catalyzed conversion of PNPP to PNP and phosphate?

61.

In terms of collision theory, to which of the following is the rate of a chemical reaction proportional?

a. the change in free energy per second
b. the change in temperature per second
c. the number of collisions per second
d. the number of product molecules

62.

Hydrogen iodide, HI, decomposes in the gas phase to produce hydrogen, H_2, and iodine, I_2. The value of the rate constant, *k*, for the reaction was measured at several different temperatures and the data are shown here:

Temperature (K)	*k* (L mol^{-1} s^{-1})
555	6.23 10^{-7}
575	2.42 10^{-6}
645	1.44 10^{-4}
700	2.01 10^{-3}

What is the value of the activation energy (in kJ/mol) for this reaction?

63.

The element Co exists in two oxidation states, Co(II) and Co(III), and the ions form many complexes. The rate at which one of the complexes of Co(III) was reduced by Fe(II) in water was measured. Determine the activation energy of the reaction from the following data:

T (K)	*k* (s^{-1})
293	0.054
298	0.100

64.

The hydrolysis of the sugar sucrose to the sugars glucose and fructose,

follows a first-order rate law for the disappearance of sucrose: rate = $k[C_{12}H_{22}O_{11}]$ (The products of the reaction, glucose and fructose, have the same molecular formulas but differ in the arrangement of the atoms in their molecules.)

a. In neutral solution, $k = 2.1\ 10^{-11}\ s^{-1}$ at 27 °C and $8.5\ 10^{-11}\ s^{-1}$ at 37 °C. Determine the activation energy, the frequency factor, and the rate constant for this equation at 47 °C (assuming the kinetics remain consistent with the Arrhenius equation at this temperature).
b. When a solution of sucrose with an initial concentration of 0.150 *M* reaches equilibrium, the concentration of sucrose is $1.65\ 10^{-7}$ *M*. How long will it take the solution to reach equilibrium at 27 °C in the absence of a catalyst? Because the concentration of sucrose at equilibrium is so low, assume that the reaction is irreversible.
c. Why does assuming that the reaction is irreversible simplify the calculation in part (b)?

65.

Use the PhET Reactions & Rates interactive simulation to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first reaction (A is yellow, B is purple, and C is navy blue). Using the “straight shot” default option, try launching the *A* atom with varying amounts of energy. What changes when the Total Energy line at launch is below the transition state of the Potential Energy line? Why? What happens when it is above the transition state? Why?

66.

Use the PhET Reactions & Rates interactive simulation to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first reaction (A is yellow, B is purple, and C is navy blue). Using the “angled shot” option, try launching the *A* atom with varying angles, but with more Total energy than the transition state. What happens when the *A* atom hits the *BC* molecule from different directions? Why?

67.

Why are elementary reactions involving three or more reactants very uncommon?

68.

In general, can we predict the effect of doubling the concentration of *A* on the rate of the overall reaction ? Can we predict the effect if the reaction is known to be an elementary reaction?

69.

Define these terms:

a. unimolecular reaction
b. bimolecular reaction
c. elementary reaction
d. overall reaction

70.

What is the rate law for the elementary termolecular reaction For

71.

Given the following reactions and the corresponding rate laws, in which of the reactions might the elementary reaction and the overall reaction be the same?

72.

Write the rate law for each of the following elementary reactions:

a.
b.
c.
d.
e.

73.

Nitrogen monoxide, NO, reacts with hydrogen, H_2, according to the following equation:

What would the rate law be if the mechanism for this reaction were:

74.

Experiments were conducted to study the rate of the reaction represented by this equation.[2]

Initial concentrations and rates of reaction are given here.

Experiment	Initial Concentration [NO] (mol L^{-1})	Initial Concentration, [H_2] (mol L^{-1} min^{-1})	Initial Rate of Formation of N_2 (mol L^{-1} min^{-1})
1	0.0060	0.0010	$1.8\ 10^{-4}$
2	0.0060	0.0020	$3.6\ 10^{-4}$
3	0.0010	0.0060	$0.30\ 10^{-4}$
4	0.0020	0.0060	$1.2\ 10^{-4}$

Consider the following questions:

a. Step 3:

75.

The reaction of CO with Cl_2 gives phosgene ($COCl_2$), a nerve gas that was used in World War I. Use the mechanism shown here to complete the following exercises:
(fast, k_1 represents the forward rate constant, k_{-1} the reverse rate constant)
(slow, k_2 the rate constant)
(fast, k_3 the rate constant)

a. Write the overall reaction.
b. Identify all intermediates.
c. Write the rate law for each elementary reaction.
d. Write the overall rate law expression.

76.

Account for the increase in reaction rate brought about by a catalyst.

77.

Compare the functions of homogeneous and heterogeneous catalysts.

78.

Consider this scenario and answer the following questions: Chlorine atoms resulting from decomposition of chlorofluoromethanes, such as CCl_2F_2, catalyze the decomposition of ozone in the atmosphere. One simplified mechanism for the decomposition is:

(a) Explain why chlorine atoms are catalysts in the gas-phase transformation:

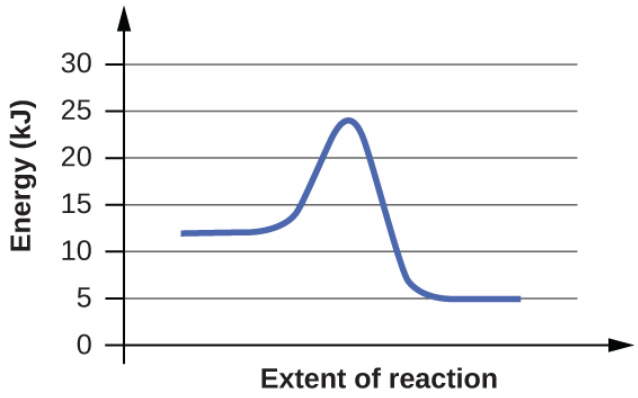
(b) Nitric oxide is also involved in the decomposition of ozone by the mechanism:

Is NO a catalyst for the decomposition? Explain your answer.

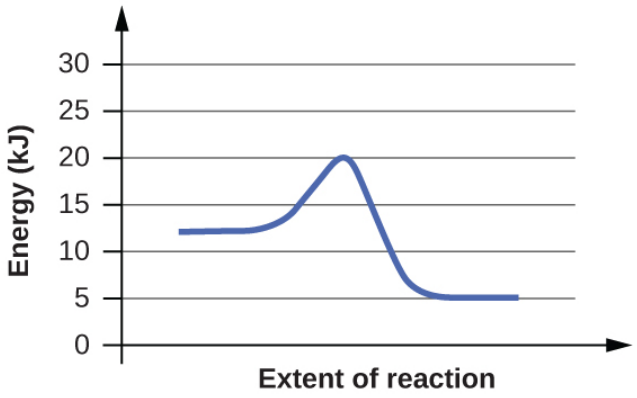
79.

For each of the following pairs of reaction diagrams, identify which of the pair is catalyzed:

(a)

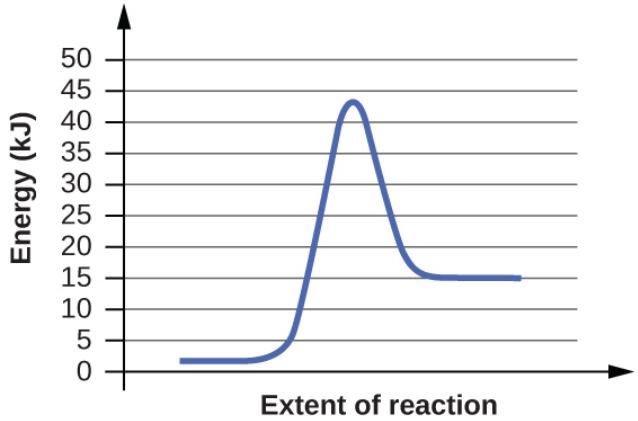


(a)

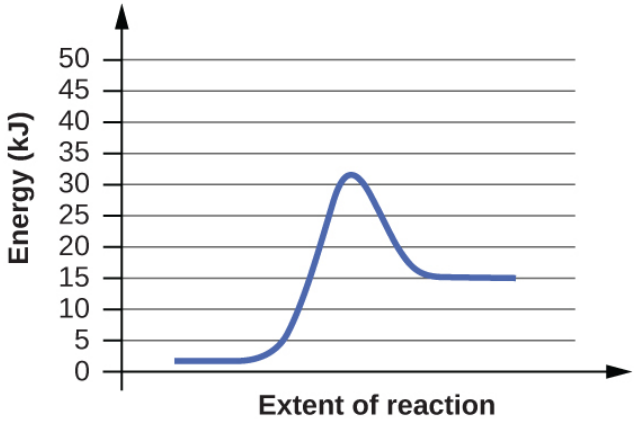


(b)

(b)



(a)

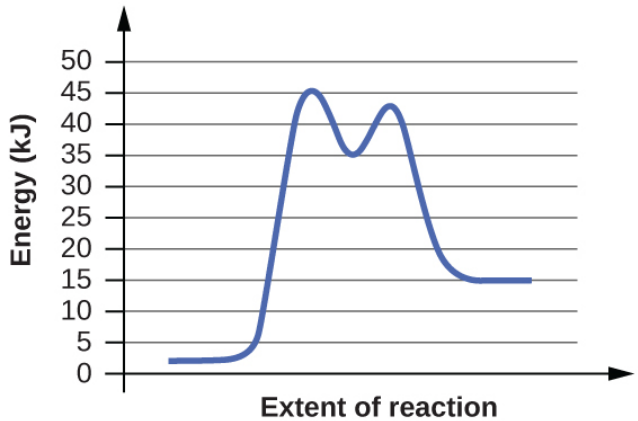


(b)

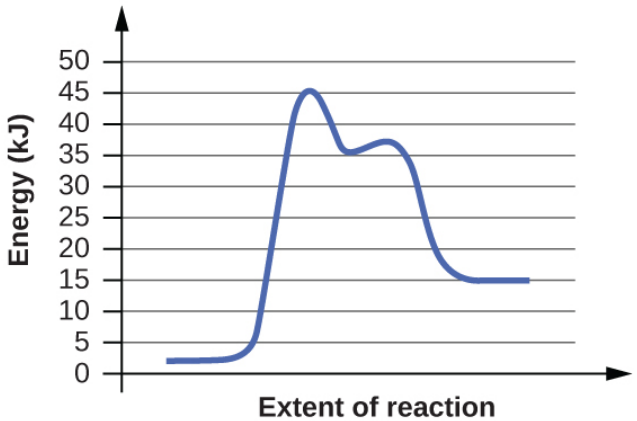
80.

For each of the following pairs of reaction diagrams, identify which of the pairs is catalyzed:

(a)

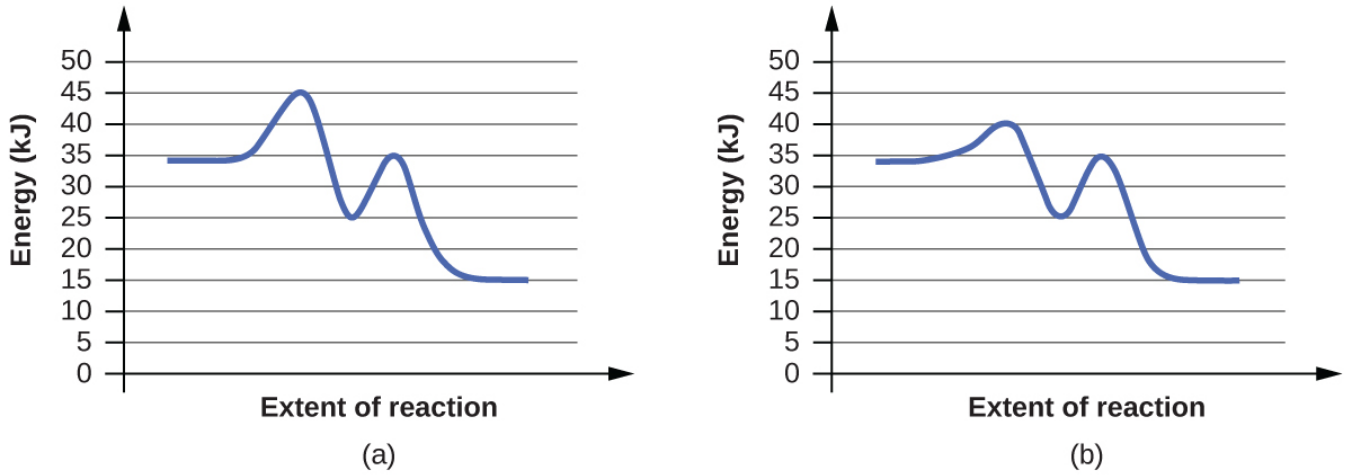


(a)



(b)

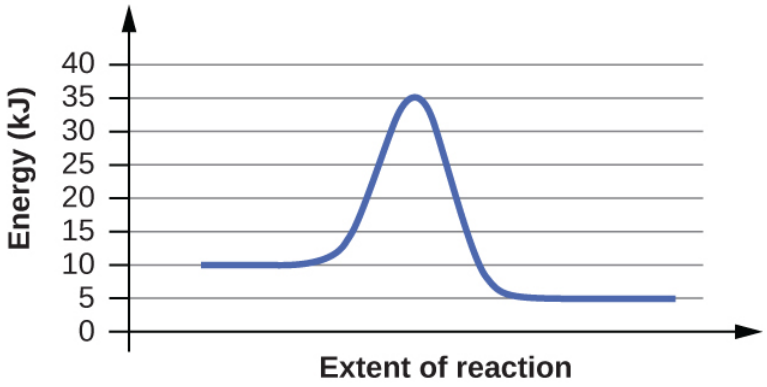
(b)



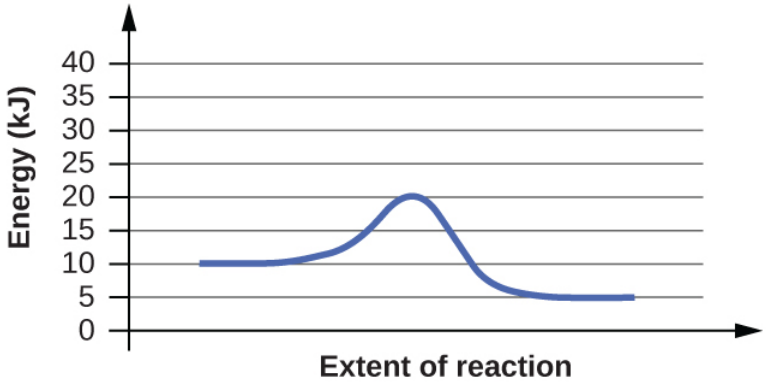
81.

For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



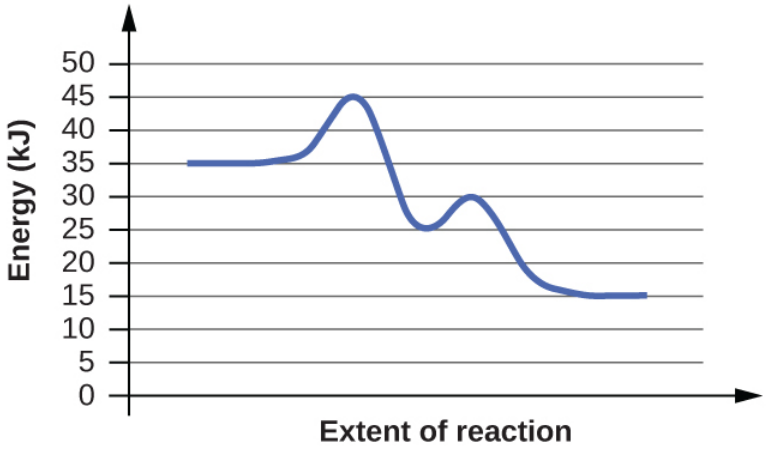
(b)



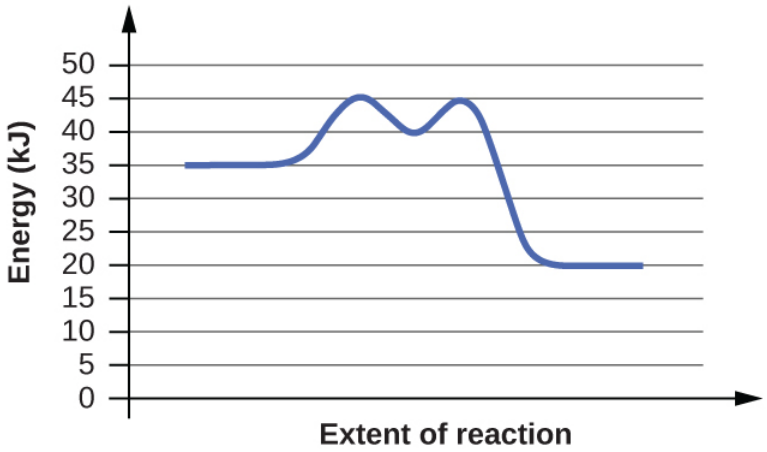
82.

For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



(b)



83.

Assuming the diagrams in Exercise 12.81 represent different mechanisms for the same reaction, which of the reactions has the faster rate?

84.

Consider the similarities and differences in the two reaction diagrams shown in Exercise 12.82. Do these diagrams represent two different overall reactions, or do they represent the same overall reaction taking place by two different mechanisms? Explain your answer.

Footnotes

- 2This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

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12.4: Chemical Reaction Rates

Learning Objectives

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

- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data

A *rate* is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The **rate of reaction** is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. For example, the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution changes slowly over time as it decomposes according to the equation:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\begin{aligned} H_2O_2 &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ \text{rate of decomposition of} \qquad &= -\frac{[H_2O_2]_{t_2} - [H_2O_2]_{t_1}}{t_2 - t_1} \\ &= -\frac{\Delta[H_2O_2]}{\Delta t} \end{aligned}$$

This mathematical representation of the change in species concentration over time is the **rate expression** for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates "change in." Thus, $[\mathrm{H_2O_2}]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time t_1; likewise, $[\mathrm{H_2O_2}]_{t_2}$ represents the molar concentration of hydrogen peroxide at a later time t2; and Δ[H2O2] represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[\mathrm{H_2O_2}]$ is a negative quantity. Reaction rates are, by convention, positive quantities, and so this negative change in concentration is multiplied by −1. Figure 12.4.1provides an example of data collected during the decomposition of $\mathrm{H_2O_2}$.

Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol L^{-1} h^{-1})
0.00	1.000			
		−0.500	6.00	0.0833
6.00	0.500			
		−0.250	6.00	0.0417
12.00	0.250			
		−0.125	6.00	0.0208
18.00	0.125			
		−0.062	6.00	0.010
24.00	0.0625			

Figure 12.4.1: The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases.

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$\frac{-\Delta\left[H_2O_2\right]}{\Delta t}=\frac{-(0.500mol/L-1.000mol/L)}{(6.00h-0.00h)}=0.0833molL^{-1}h^{-1}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

$$\frac{-\Delta\left[H_2O_2\right]}{\Delta t}=\frac{-(0.0625mol/L-0.125mol/L)}{(24.00h-18.00h)}=0.010molL^{-1}h^{-1}$$

This behavior indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an **average rate** for the reaction over this time interval. At any specific time, the rate at which a reaction is proceeding is known as its **instantaneous rate**. The instantaneous rate of a reaction at "time zero," when the reaction commences, is its **initial rate**. Consider the analogy of a car slowing down as it approaches a stop sign. The vehicle's initial rate—analogous to the beginning of a chemical reaction—would be the speedometer reading at the moment the driver begins pressing the brakes (t_0). A few moments later, the instantaneous rate at a specific moment—call it t_1—would be somewhat slower, as indicated by the speedometer reading at that point in time. As time passes, the instantaneous rate will continue to fall until it reaches zero, when the car (or reaction) stops. Unlike instantaneous speed, the car's average speed is not indicated by the speedometer; but it can be calculated as the ratio of the distance traveled to the time required to bring the vehicle to a complete stop (Δt). Like the decelerating car, the average rate of a chemical reaction will fall somewhere between its initial and final rates.

The instantaneous rate of a reaction may be determined one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible. In a plot of the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of H_2O_2 at any time t is given by the slope of a straight line that is tangent to the curve at that time (Figure 12.4.2). These tangent line slopes may be evaluated using calculus, but the procedure for doing so is beyond the scope of this chapter.

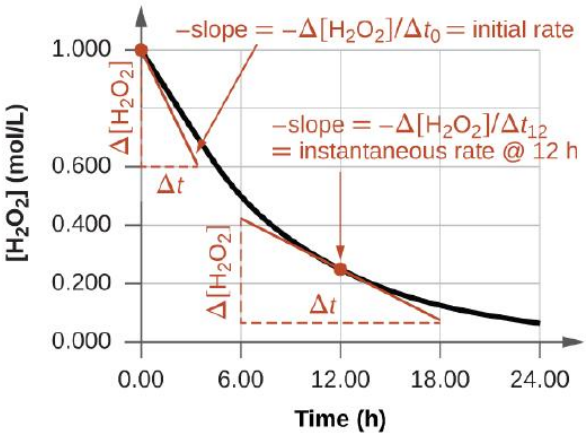


Figure 12.4.2: This graph shows a plot of concentration versus time for a 1.000 *M* solution of H_2O_2. The rate at any time is equal to the negative of the slope of a line tangent to the curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 12 h ("instantaneous rate" at 12 h).

Chemistry in Everyday Life: Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (Figure 12.4.3). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in color upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:

$$C_6H_{12}O_6 + O_2 \xrightarrow{\text{catalyst}} C_6H_{10}O_6 + H_2O_2$$

$$2H_2O_2 + 2I^- \xrightarrow{\text{catalyst}} I_2 + 2H_2O + O_2$$

The first equation depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine, which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change.

The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis*, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the color-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the color change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.

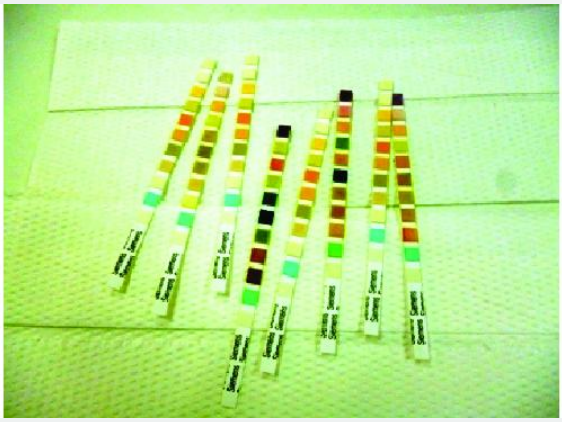


Figure 12.4.3: Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman)

Relative Rates of Reaction

The rate of a reaction may be expressed as the change in concentration of any reactant or product. For any given reaction, these rate expressions are all related simply to one another according to the reaction stoichiometry. The rate of the general reaction

$$A \longrightarrow B \tag{12.4.1}$$

can be expressed in terms of the decrease in the concentration of A or the increase in the concentration of B. These two rate expressions are related by the stoichiometry of the reaction:

$$\text{rate} = -\left(\frac{1}{a}\right)\left(\frac{\Delta A}{\Delta t}\right) = \left(\frac{1}{b}\right)\left(\frac{\Delta B}{\Delta t}\right)$$

Consider the reaction represented by the following equation:

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

The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta mol\ NH_3}{\Delta t} \times \frac{1 mol\ N_2}{2 mol\ NH_3} = \frac{\Delta mol\ N_2}{\Delta t}$$

This may be represented in an abbreviated format by omitting the units of the stoichiometric factor:

$$-\frac{1}{2}\frac{\Delta mol\ NH_3}{\Delta t} = \frac{\Delta mol\ N_2}{\Delta t}$$

Note that a negative sign has been included as a factor to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). For homogeneous reactions, both the reactants and products are present in the same solution and thus occupy the same volume, so the molar amounts may be replaced with molar concentrations:

$$-\frac{1}{2}\frac{\Delta\left[NH_3\right]}{\Delta t}=\frac{\Delta\left[N_2\right]}{\Delta t}$$

Similarly, the rate of formation of H_2 is three times the rate of formation of N_2 because three moles of H_2 are produced for each mole of N_2 produced.

$$\frac{1}{3}\frac{\Delta\left[H_2\right]}{\Delta t}=\frac{\Delta\left[N_2\right]}{\Delta t}$$

Figure 12.4.4 illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. Slopes of the tangent lines at t = 500 s show that the instantaneous rates derived from all three species involved in the reaction are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

$$\frac{2.91\times10^{-6}M/s}{9.70\times10^{-7}M/s}\approx3$$

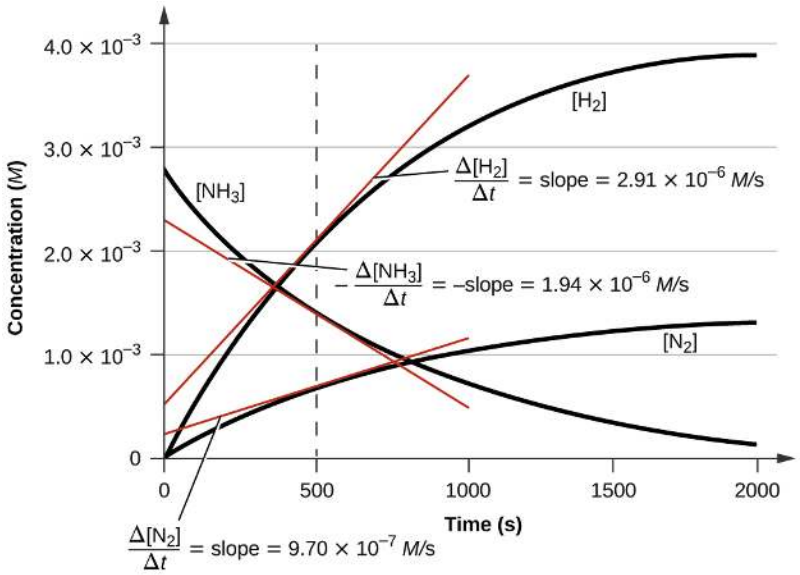


Figure 12.4.4: Changes in concentrations of the reactant and products for the reaction $2\,\mathrm{NH_3} \longrightarrow \mathrm{N_2} + 3\,\mathrm{H_2}$. The rates of change of the three concentrations are related by the reaction stoichiometry, as shown by the different slopes of the tangents at t = 500 s.

Example 12.4.1: Expressions for Relative Reaction Rates

The first step in the production of nitric acid is the combustion of ammonia:

$$4NH_3(g)+5O_2(g)\longrightarrow4NO(g)+6H_2O(g) \tag{12.4.2}$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Solution

Considering the stoichiometry of this homogeneous reaction, the rates for the consumption of reactants and formation of products are:

$$-\frac{1}{4}\frac{\Delta\left[NH_3\right]}{\Delta t}=-\frac{1}{5}\frac{\Delta\left[O_2\right]}{\Delta t}=\frac{1}{4}\frac{\Delta[NO]}{\Delta t}=\frac{1}{6}\frac{\Delta\left[H_2O\right]}{\Delta t}$$

Exercise 12.4.1

The rate of formation of Br_2 is 6.0 10^{-6} mol/L/s in a reaction described by the following net ionic equation:

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Answer

$$-\frac{1}{5}\frac{\Delta\left[Br^-\right]}{\Delta t} = -\frac{\Delta\left[BrO_3^-\right]}{\Delta t} = -\frac{1}{6}\frac{\Delta\left[H^+\right]}{\Delta t} = \frac{1}{3}\frac{\Delta\left[Br_2\right]}{\Delta t} = \frac{1}{3}\frac{\Delta\left[H_2O\right]}{\Delta t}$$

Example 12.4.2: Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure 12.4.2 shows the rate of the decomposition of H_2O_2 over time:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Based on these data, the instantaneous rate of decomposition of H_2O_2 at t = 11.1 h is determined to be 3.20 10^{-2} mol/L/h, that is:

$$-\frac{1}{2}\frac{\Delta\left[\mathrm{H_2O_2}\right]}{\Delta t} = \frac{1}{2}\frac{\Delta\left[\mathrm{H_2O}\right]}{\Delta t} = \frac{\Delta\left[\mathrm{O_2}\right]}{\Delta t} \tag{12.4.3}$$

What is the instantaneous rate of production of $\mathrm{H_2O}$ and $\mathrm{O_2}$?

Solution

The reaction stoichiometry shows that

$$-\frac{1}{2}\frac{\Delta\left[\mathrm{H_2O_2}\right]}{\Delta t} = \frac{1}{2}\frac{\Delta\left[\mathrm{H_2O}\right]}{\Delta t} = \frac{\Delta\left[\mathrm{O_2}\right]}{\Delta t} \tag{12.4.4}$$

Therefore:

$$\frac{1}{2} \times 3.20 \times 10^{-2} molL^{-1}h^{-1} = \frac{\Delta\left[O_2\right]}{\Delta t}$$

and

$$\frac{\Delta\left[O_2\right]}{\Delta t} = 1.60 \times 10^{-2} molL^{-1}h^{-1}$$

Exercise 12.4.2

If the rate of decomposition of ammonia, NH_3, at 1150 K is 2.10 10^{-6} mol/L/s, what is the rate of production of nitrogen and hydrogen?

Answer

1.05 10^{-6} mol/L/s, N_2 and 3.15 10^{-6} mol/L/s, H_2.

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12.5: Factors Affecting Reaction Rates

Learning Objectives

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

- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. Five factors typically affecting the rates of chemical reactions will be explored in this section: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

The Physical States of the Reactants

A chemical reaction between two or more substances requires intimate contact between the reactants. When reactants are in different physical states, or phases (solid, liquid, gaseous, dissolved), the reaction takes place only at the interface between the phases. Consider the heterogeneous reaction between a solid phase and either a liquid or gaseous phase. Compared with the reaction rate for large solid particles, the rate for smaller particles will be greater because the surface area in contact with the other reactant phase is greater. For example, large pieces of iron react more slowly with acids than they do with finely divided iron powder (Figure 12.5.1). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.



Figure 12.5.1: (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas: $2Fe(s) + 6HCl(aq)\ 2FeCl_3(aq) + 3H_2(g)$. (b) An iron nail reacts more slowly because the surface area exposed to the acid is much less.

Link to Learning

Watch this video to see the reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.

Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. Gas burners, hot plates, and ovens are often used in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. For many chemical processes, reaction rates are approximately doubled when the temperature is raised by 10 °C.

Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate ($CaCO_3$) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (Figure 12.5.2). An acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$\mathrm{SO_2(g) + H_2O(g) \longrightarrow H_2SO_3(aq)}$$

Calcium carbonate reacts with sulfurous acid as follows:

$$\mathrm{CaCO_3(s) + H_2SO_3(aq) \longrightarrow CaSO_3(aq) + CO_2(g) + H_2O(l)}$$

In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.



Figure 12.5.2: Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III)

Link to Learning

Phosphorus burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen is higher. Watch this video to see an example.

The Presence of a Catalyst

Relatively dilute aqueous solutions of hydrogen peroxide, $\mathrm{H_2O_2}$, are commonly used as topical antiseptics. Hydrogen peroxide decomposes to yield water and oxygen gas according to the equation:

$$\mathrm{2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g)}$$

Under typical conditions, this decomposition occurs very slowly. When dilute $\mathrm{H_2O_2(aq)}$ is poured onto an open wound, however, the reaction occurs rapidly and the solution foams because of the vigorous production of oxygen gas. This dramatic difference is caused by the presence of substances within the wound's exposed tissues that accelerate the decomposition process. Substances that function to increase the rate of a reaction are called **catalysts**, a topic treated in greater detail later in this chapter.

Link to Learning

Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the PhET Reactions & Rates interactive to explore how temperature, concentration, and the nature of the reactants affect reaction rates.

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12.6: Rate Laws

Learning Objectives

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

- Explain the form and function of a rate law
- Use rate laws to calculate reaction rates
- Use rate and concentration data to identify reaction orders and derive rate laws

As described in the previous module, the rate of a reaction is often affected by the concentrations of reactants. Rate laws (sometimes called *differential rate laws*) or rate equations are mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants. As an example, consider the reaction described by the chemical equation

$$aA + bB \longrightarrow \text{ products}$$

where a and b are stoichiometric coefficients. The rate law for this reaction is written as:

$$\text{rate } = k[A]^m[B]^n$$

in which [*A*] and [*B*] represent the molar concentrations of reactants, and *k* is the **rate constant**, which is specific for a particular reaction at a particular temperature. The exponents *m* and *n* are the **reaction orders** and are typically positive integers, though they can be fractions, negative, or zero. The rate constant *k* and the reaction orders *m* and *n* must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. The rate constant *k* is independent of the reactant concentrations, but it does vary with temperature.

The reaction orders in a rate law describe the mathematical dependence of the rate on reactant concentrations. Referring to the generic rate law above, the reaction is *m* order with respect to *A* and *n* order with respect to *B*. For example, if *m* = 1 and *n* = 2, the reaction is first order in *A* and second order in *B*. The overall reaction order is simply the sum of orders for each reactant. For the example rate law here, the reaction is third order overall (1 + 2 = 3). A few specific examples are shown below to further illustrate this concept.

The rate law:

$$\text{rate } = k\left[H_2O_2\right]$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate } = k\left[\mathrm{C_4H_6}\right]^2$$

describes a reaction that is second order in $\mathrm{C_4H_6}$ and second order overall. The rate law:

$$\text{rate } = k\left[\mathrm{H^+}\right]\left[\mathrm{OH^-}\right]$$

describes a reaction that is first order in $\mathrm{H^+}$, first order in $\mathrm{OH^-}$, and second order overall.

Example 12.6.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\mathrm{NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)}$$

is second order in $\mathrm{NO_2}$ and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate } = k[\mathrm{NO_2}]^m[\mathrm{CO}]^n$$

The reaction is second order in $\mathrm{NO_2}$; thus $m = 2$. The reaction is zero order in CO; thus $n = 0$. The rate law is:

$$\text{rate} = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[\text{CO}]^0 = 1$, which is why the CO concentration term may be omitted from the rate law: the rate of reaction is solely dependent on the concentration of NO_2. A later chapter section on reaction mechanisms will explain how a reactant's concentration can have no effect on a reaction rate despite being involved in the reaction.

? Exercise 12.6.1A

The rate law for the reaction:

$$\text{H}_2(\text{g}) + 2\,\text{NO}(\text{g}) \longrightarrow \text{N}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g})$$

has been determined to be rate = k[NO]^2[H_2]. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer

order in NO = 2; order in H_2 = 1; overall order = 3

? Exercise 12.6.1B

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($\text{CH}_3\text{CH}_2\text{OCOCH}_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$\text{CH}_3\text{OH} + \text{CH}_3\text{CH}_2\text{OCOCH}_3 \longrightarrow \text{CH}_3\text{OCOCH}_3 + \text{CH}_3\text{CH}_2\text{OH}$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, determined to be:

$$\text{rate} = k\left[\text{CH}_3\text{OH}\right]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

order in CH_3OH = 1; order in $CH_3CH_2OCOCH_3$ = 0; overall order = 1

A common experimental approach to the determination of rate laws is the **method of initial rates**. This method involves measuring reaction rates for multiple experimental trials carried out using different initial reactant concentrations. Comparing the measured rates for these trials permits determination of the reaction orders and, subsequently, the rate constant, which together are used to formulate a rate law. This approach is illustrated in the next two example exercises.

✓ Example 12.6.2: Determining a Rate Law from Initial Rates

Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica (Figure 12.6.1). One such reaction is the combination of nitric oxide, NO, with ozone, O_3:

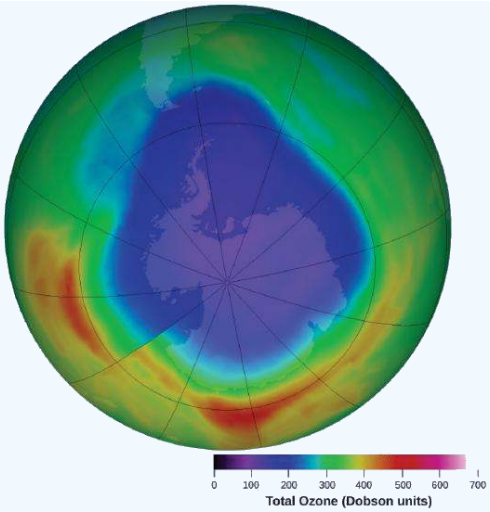


Figure 12.6.1: A contour map showing stratospheric ozone concentration and the “ozone hole” that occurs over Antarctica during its spring months. (credit: modification of work by NASA)

$$\mathrm{NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)}$$

This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	[NO] (mol/L)	[O_3] (mol/L)	$\frac{\Delta[NO_2]}{\Delta t}(\mathrm{molL^{-1}s^{-1}})$
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
3	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
4	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
5	3.00×10^{-6}	9.00×10^{-6}	5.94×10^{-4}

Determine the rate law and the rate constant for the reaction at 25 °C.

Solution

The rate law will have the form:

$$\text{rate } = k[NO]^m[O_3]^n$$

Determine the values of *m*, *n*, and *k* from the experimental data using the following three-part process:

Step 1:

Determine the value of m *from the data in which [NO] varies and [O_3] is constant.* In the last three experiments, [NO] varies while [O_3] remains constant. When [NO] doubles from trial 3 to 4, the rate doubles, and when [NO] triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to [NO], and *m* in the rate law is equal to 1.

Step 2:

Determine the value of n *from data in which [O_3] varies and [NO] is constant.* In the first three experiments, [NO] is constant and [O_3] varies. The reaction rate changes in direct proportion to the change in [O_3]. When [O_3] doubles from trial 1 to 2, the rate doubles; when [O_3] triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to [O_3], and *n* is equal to 1.The rate law is thus:

$$\text{rate } = k[NO]^1[O_3]^1 = k[NO]\,[O_3]$$

Step 3:

Determine the value of k *from one set of concentrations and the corresponding rate*. The data from trial 1 are used below:

$$k = \frac{\text{rate}}{[\text{NO}]\,[\text{O}_3]}$$

$$= \frac{6.60 \times 10^{-5}\ \text{mol L}^{-1}\text{s}^{-1}}{\left(1.00 \times 10^{-6}\ \text{mol L}^{-1}\right)\left(3.00 \times 10^{-6}\ \text{mol L}^{-1}\right)}$$

$$= 2.20 \times 10^{7}\ \text{L mol}^{-1}\text{s}^{-1}$$

Exercise 12.6.2

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

$$\text{CH}_3\text{CHO(g)} \longrightarrow \text{CH}_4\text{(g)} + \text{CO(g)}$$

Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	[CH3CHO] (mol/L)	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}(\text{mol L}^{-1}\text{s}^{-1})$
1	1.75×10^{-3}	2.06×10^{-11}
2	3.50×10^{-3}	8.24×10^{-11}
3	7.00×10^{-3}	3.30×10^{-10}

Answer

$\text{rate} = k\left[\text{CH}_3\text{CHO}\right]^2$ with k = 6.7310^{-6} L/mol/s

Example 12.6.3: Determining Rate Laws from Initial Rates

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

Trial	[NO] (mol/L)	[Cl2] (mol/L)	$-\frac{\Delta[\text{CO}]}{\Delta t}(\text{mol } L^{-1}\text{s}^{-1})$
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Solution

The rate law for this reaction will have the form:

$$\text{rate} = k[NO]^m[Cl_2]^n$$

As in Example 12.6.2, approach this problem in a stepwise fashion, determining the values of *m* and *n* from the experimental data and then using these values to determine the value of *k*. In this example, however, an explicit algebraic approach (vs. the implicit approach of the previous example) will be used to determine the values of *m* and *n*:

Step 1

Determine the value of m from the data in which $[\text{NO}]$ varies and $[\text{Cl}_2]$ is constant. Write the ratios with the subscripts x and y to indicate data from two different trials:

$$\frac{\text{rate}_x}{\text{rate}_y} = \frac{k[NO]_x^m[Cl_2]_x^n}{k[NO]_y^m[Cl_2]_y^n}$$

Using the third trial and the first trial, in which $[Cl_2]$ does not vary, gives:

$$\frac{\text{rate } 3}{\text{rate } 1} = \frac{0.00675}{0.00300} = \frac{k(0.15)^m(0.10)^n}{k(0.10)^m(0.10)^n}$$

Canceling equivalent terms in the numerator and denominator leaves:

$$\frac{0.00675}{0.00300} = \frac{(0.15)^m}{(0.10)^m}$$

which simplifies to:

$$2.25 = (1.5)^m$$

Use logarithms to determine the value of the exponent *m*:

$$\ln(2.25) = m\ln(1.5)$$

$$\frac{\ln(2.25)}{\ln(1.5)} = m$$

$$2 = m$$

Confirm the result

$$1.5^2 = 2.25$$

Step 2

Determine the value of n from data in which $[Cl_2]$ varies and $[NO]$ is constant.

$$\frac{\text{rate } 2}{\text{rate } 1} = \frac{0.00450}{0.00300} = \frac{k0.10)^m(0.15)^n}{k(0.10)^m(0.10)^n}$$

Cancelation gives:

$$\frac{0.0045}{0.0030} = \frac{(0.15)^n}{(0.10)^n}$$

which simplifies to:

$$1.5 = (1.5)^n$$

Thus n must be 1, and the form of the rate law is:

$$\text{rate } = k[NO]^m[Cl_2]^n = k[NO]^2\,[Cl_2]$$

Step 3.

Determine the numerical value of the constant with appropriate units. The units for the rate of a reaction are mol/L/s. The units for are whatever is needed so that substituting into the rate law expression affords the appropriate units for the rate. In this example, the concentration units are mol^3/L^3. The units for *k* should be mol^- L/s so that the rate is in terms of mol/L/s.

To determine the value of *k* once the rate law expression has been solved, simply plug in values from the first experimental trial and solve for *k*:

$$0.00300 \text{ mol L}^{-1}\text{s}^{-1} = k\left(0.10 \text{ mol L}^{-1}\right)^2\left(0.10 \text{ mol L}^{-1}\right)^1$$

$$k = 3.0 \text{ mol}^{-2}\text{L}^2\text{s}^{-1}$$

Exercise 12.6.3

Use the provided initial rate data to derive the rate law for the reaction whose equation is:

$$\mathrm{OCl^-(aq) + I^-(aq) \longrightarrow OI^-(aq) + Cl^-(aq)}$$

Trial	$[OCl^-]$ (mol/L)	$[I^-]$ (mol/L)	Initial Rate (mol/L/s)
1	0.0040	0.0020	0.00184
2	0.0020	0.0040	0.00092
3	0.0020	0.0020	0.00046

Determine the rate law expression and the value of the rate constant k with appropriate units for this reaction.

Answer

$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{0.00092}{0.00046} = \frac{k(0.0020)^x(0.0040)^y}{k(0.0020)^x(0.0020)^y}$$

$$2.00 = 2.00^y$$

$$y = 1$$

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{0.00184}{0.00092} = \frac{k(0.0040)^x(0.0020)^y}{k(0.0020)^x(0.0040)^y}$$

$$2.00 = \frac{2^x}{2^y}$$

$$2.00 = \frac{2^x}{2^1}$$

$$4.00 = 2^x$$

$$x = 2$$

Substituting the concentration data from trial 1 and solving for k yields:

$$\text{rate } = k\left[OCl^-\right]^2\left[I^-\right]^1$$

$$0.00184 = k(0.0040)^2(0.0020)^1$$

$$k = 5.75 \times 10^4 mol^{-2}L^2s^{-1}$$

Reaction Order and Rate Constant Units

In some of our examples, the reaction orders in the rate law happen to be the same as the coefficients in the chemical equation for the reaction. This is merely a coincidence and very often not the case.

Rate laws may exhibit fractional orders for some reactants, and negative reaction orders are sometimes observed when an increase in the concentration of one reactant causes a decrease in reaction rate. A few examples illustrating these points are provided:

$$\mathrm{NO_2 + CO \longrightarrow NO + CO_2} \qquad \text{rate } = k[NO_2]^2$$

$$\mathrm{CH_3CHO \longrightarrow CH_4 + CO} \qquad \text{rate } = k[CH_3CHO]^2$$

$$\mathrm{2\,N_2O_5 \longrightarrow NO_2 + O_2} \qquad \text{rate } = k\left[N_2O_5\right]$$

$$\mathrm{2\,NO_2 + F_2 \longrightarrow 2\,NO_2F} \qquad \text{rate } = k\left[NO_2\right]\left[F_2\right]$$

$$\mathrm{2\,NO_2Cl \longrightarrow 2\,NO_2 + Cl_2} \qquad \text{rate } = k\left[NO_2Cl\right]$$

Note

It is important to note that *rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

The units for a rate constant will vary as appropriate to accommodate the overall order of the reaction. The unit of the rate constant for the second-order reaction described in Example 12.6.2 was determined to be k was derived to be $\mathrm{L\,mol^{-1}s^{-1}}$. For the third-order reaction, k was derived to be $\mathrm{L^2mol^{-2}s^{-1}}$. Dimensional analysis requires the rate constant unit for a reaction whose overall order is x to be $\mathrm{L^{x-1}\ mol^{1-x}s^{-1}}$. Table 12.6.1 summarizes the rate constant units for common reaction orders.

Table 12.6.1: Rate Constant Units for Common Reaction Orders

Overall Reaction Order (x)	Rate Constant Unit ($\mathrm{L^{x-1}\ mol^{1-x}\ s^{-1}}$)
0 (zero)	$\mathrm{mol\ L^{-1}\ s^{-1}}$
1 (first)	$\mathrm{s^{-1}}$
2 (second)	$\mathrm{L\ mol^{-1}\ s^{-1}}$
3 (third)	$\mathrm{L^2\ mol^{-2}\ s^{-1}}$

Note that the units in this table were derived using specific units for concentration (mol/L) and time (s), though any valid units for these two properties may be used.

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12.7: Integrated Rate Laws

Learning Objectives

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

- Explain the form and function of an integrated rate law
- Perform integrated rate law calculations for zero-, first-, and second-order reactions
- Define half-life and carry out related calculations
- Identify the order of a reaction from concentration/time data

The rate laws discussed thus far relate the rate and the concentrations of reactants. We can also determine a second form of each rate law that relates the concentrations of reactants and time. These are called **integrated rate laws**. We can use an integrated rate law to determine the amount of reactant or product present after a period of time or to estimate the time required for a reaction to proceed to a certain extent. For example, an integrated rate law is used to determine the length of time a radioactive material must be stored for its radioactivity to decay to a safe level.

Using calculus, the differential rate law for a chemical reaction can be integrated with respect to time to give an equation that relates the amount of reactant or product present in a reaction mixture to the elapsed time of the reaction. This process can either be very straightforward or very complex, depending on the complexity of the differential rate law. For purposes of discussion, we will focus on the resulting integrated rate laws for first-, second-, and zero-order reactions.

First-Order Reactions

Integration of the rate law for a simple first-order reaction (rate = $k[A]$) results in an equation describing how the reactant concentration varies with time:

$$[A]_t = [A]_0 e^{-kt}$$

where $[A]t$ is the concentration of A at any time t, $[A]_0$ is the initial concentration of A, and k is the first-order rate constant.

For mathematical convenience, this equation may be rearranged to other formats, including direct and indirect proportionalities:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

or

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

and a format showing a linear dependence of concentration in time:

$$\ln[A]_t = \ln[A]_0 - kt$$

Example 12.7.1: The Integrated Rate Law for a First-Order Reaction

The rate constant for the first-order decomposition of cyclobutane, C_4H_8 at 500 °C is 9.2 10^{-3} s^{-1}:

$$C_4H_8 \longrightarrow 2\,C_2H_4$$

How long will it take for 80.0% of a sample of C_4H_8 to decompose?

Solution

Since the relative change in reactant concentration is provided, a convenient format for the integrated rate law is:

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

The initial concentration of C_4H_8, $[A]_0$, is not provided, but the provision that 80.0% of the sample has decomposed is enough information to solve this problem. Let x be the initial concentration, in which case the concentration after 80.0% decomposition

is 20.0% of *x* or 0.200*x*. Rearranging the rate law to isolate *t* and substituting the provided quantities yields:

$$\begin{aligned} t &= \ln \frac{[x]}{[0.200x]} \times \frac{1}{k} \\ &= \ln 5 \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\ &= 1.609 \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\ &= 1.7 \times 10^{2}\ \text{s} \end{aligned}$$

Exercise 12.7.1

Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131 according to the equation:

$$\text{I-131} \longrightarrow \text{Xe-131} + \text{electron}$$

The decay is first-order with a rate constant of 0.138 d^{-1}. How many days will it take for 90% of the iodine−131 in a 0.500 *M* solution of this substance to decay to Xe-131?

Answer

16.7 days

In the next example exercise, a linear format for the integrated rate law will be convenient:

$$\begin{aligned} \ln[A]_t &= (-k)(t) + \ln[A]_0 \\ y &= mx + b \end{aligned}$$

A plot of $\ln[A]_t$ versus *t* for a first-order reaction is a straight line with a slope of $-k$ and a *y*-intercept of $\ln[A]_0$. If a set of rate data are plotted in this fashion but do *not* result in a straight line, the reaction is not first order in *A*.

Example 12.7.2: Graphical Determination of Reaction Order and Rate Constant

Show that the data in Figure 12.7.1 can be represented by a first-order rate law by graphing $\ln[H_2O_2]$ versus time. Determine the rate constant for the decomposition of H_2O_2 from these data.

Solution

The data from Figure 12.7.1 are tabulated below, and a plot of $\ln[H_2O_2]$ is shown in Figure 12.7.1.

Time (h)	$[H_2O_2]$ (*M*)	$\ln[H_2O_2]$
0.00	1.000	0.000
6.00	0.500	−0.693
12.00	0.250	−1.386
18.00	0.125	−2.079
24.00	0.0625	−2.772

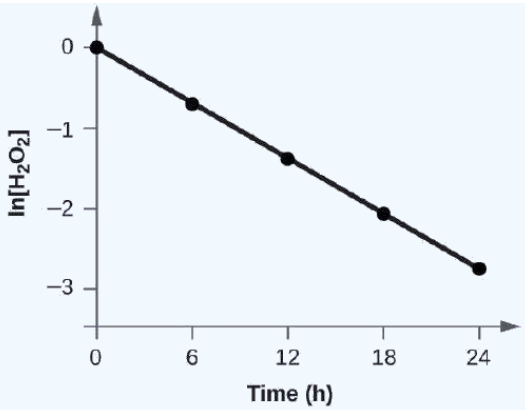


Figure 12.7.1: A linear relationship between $\ln[H_2O_2]$ and time suggests the decomposition of hydrogen peroxide is a first-order reaction.

The plot of $\ln[H_2O_2]$ versus time is linear, indicating that the reaction may be described by a first-order rate law.

According to the linear format of the first-order integrated rate law, the rate constant is given by the negative of this plot's slope.

$$\text{slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln[H_2O_2]}{\Delta t}$$

The slope of this line may be derived from two values of $\ln[H_2O_2]$ at different values of t (one near each end of the line is preferable). For example, the value of $\ln[H_2O_2]$ when t is 0.00 h is 0.000; the value when t = 24.00 h is −2.772

$$\begin{aligned}\text{slope} &= \frac{-2.772 - 0.000}{24.00 - 0.00h} \\ &= \frac{-2.772}{24.00h} \\ &= -0.116h^{-1} \\ k &= -\text{ slope} = -\left(-0.116h^{-1}\right) = 0.116h^{-1}\end{aligned}$$

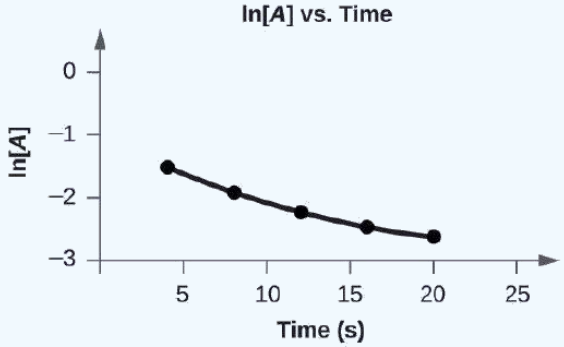
Exercise 12.7.2

Graph the following data to determine whether the reaction $A \longrightarrow B + C$ is first order.

Time (s)	[A]
4.0	0.220
8.0	0.144
12.0	0.110
16.0	0.088
20.0	0.074

Answer

The plot of $\ln[A]_t$ vs. t is not linear, indicating the reaction is not first order:



Second-Order Reactions

The equations that relate the concentrations of reactants and the rate constant of second-order reactions can be fairly complicated. To illustrate the point with minimal complexity, only the simplest second-order reactions will be described here, namely, those whose rates depend on the concentration of just one reactant. For these types of reactions, the differential rate law is written as:

$$\text{rate } = k[A]^2$$

For these second-order reactions, the integrated rate law is:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

where the terms in the equation have their usual meanings as defined earlier.

Example 12.7.3: The Integrated Rate Law for a Second-Order Reaction

The reaction of butadiene gas (C_4H_6) to yield C_8H_{12} gas is described by the equation:

$$2C_4H_6(g) \longrightarrow C_8H_{12}(g)$$

This "dimerization" reaction is second order with a rate constant equal to 5.76 10^{-2} L mol^{-1} min^{-1} under certain conditions. If the initial concentration of butadiene is 0.200 *M*, what is the concentration after 10.0 min?

Solution

For a second-order reaction, the integrated rate law is written

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

We know three variables in this equation: $[A]_0$ = 0.200 mol/L, k = 5.76 10^{-2} L/mol/min, and t = 10.0 min. Therefore, we can solve for $[A]$, the fourth variable:

$$\begin{aligned}\frac{1}{[A]_t} &= \left(5.76 \times 10^{-2} L mol^{-1} min^{-1}\right)(10 min) + \frac{1}{0.200 mol^{-1}} \\ &= \left(5.76 \times 10^{-1} L mol^{-1}\right) + 5.00 L mol^{-1} \\ &= 5.58 L mol^{-1} \\ [A]_t &= 1.79 \times 10^{-1} mol L^{-1}\end{aligned}$$

Therefore 0.179 mol/L of butadiene remain at the end of 10.0 min, compared to the 0.200 mol/L that was originally present.

Exercise 12.7.3

If the initial concentration of butadiene is 0.0200 *M*, what is the concentration remaining after 20.0 min?

Answer

0.0195 mol/L

The integrated rate law for second-order reactions has the form of the equation of a straight line:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$y = mx + b$$

A plot of $\frac{1}{[A]_t}$ versus t for a second-order reaction is a straight line with a slope of k and a y-intercept of $\frac{1}{[A]_0}$. If the plot is not a straight line, then the reaction is not second order.

Example 12.7.4: Graphical Determination of Reaction Order and Rate Constant

The data below are for the same reaction described in Example 12.7.3. Prepare and compare two appropriate data plots to identify the reaction as being either first or second order. After identifying the reaction order, estimate a value for the rate constant.

Solution

Time (s)	$[C_4H_6]$ (M)
0	1.00×10^{-2}
1600	5.04×10^{-3}
3200	3.37×10^{-3}
4800	2.53×10^{-3}
6200	2.08×10^{-3}

In order to distinguish a first-order reaction from a second-order reaction, prepare a plot of $\ln[C_4H_6]_t$ versus t and compare it to a plot of $\frac{1}{[C_4H_6]_t}$ versus t. The values needed for these plots follow.

Time (s)	$\frac{1}{[C_4H_6]}(M^{-1})$	$\ln[C_4H_6]$
0	100	−4.605
1600	198	−5.289
3200	296	−5.692
4800	395	−5.978
6200	481	−6.175

The plots are shown in Figure 12.7.2, which clearly shows the plot of $\ln[C_4H_6]_t$ versus t is not linear, therefore the reaction is not first order. The plot of $\frac{1}{[C_4H_6]_t}$ versus t is linear, indicating that the reaction is second order.

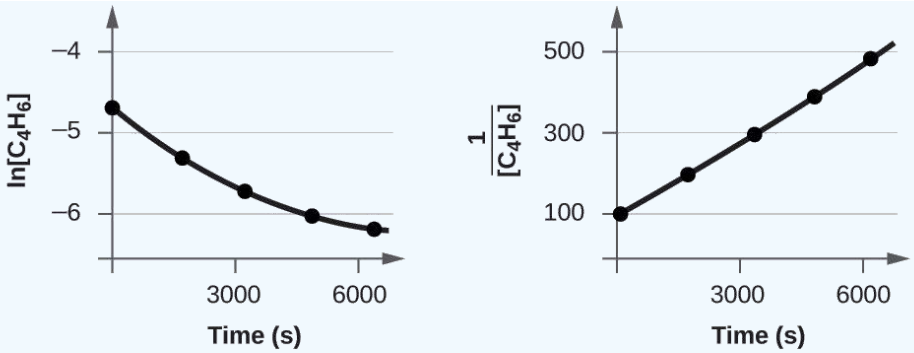


Figure 12.7.2: These two graphs show first- and second-order plots for the dimerization of C_4H_6. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

According to the second-order integrated rate law, the rate constant is equal to the slope of the versus *t* plot. Using the data for *t* = 0 *s* and *t* = 6200 *s*, the rate constant is estimated as follows:

$$k = \text{ slope } = \frac{\left(481M^{-1} - 100M^{-1}\right)}{(6200s - 0s)} = 0.0614M^{-1}s^{-1}$$

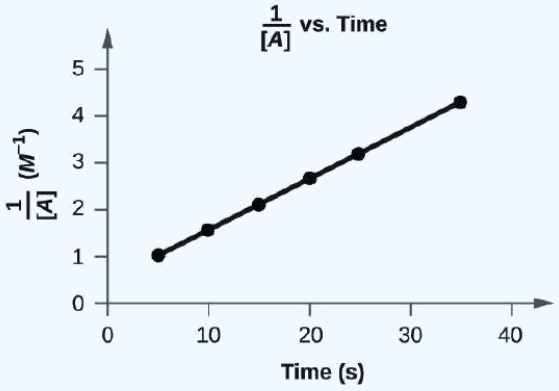
Exercise 12.7.4

Do the following data fit a second-order rate law?

Time (s)	[*A*] (*M*)
5	0.952
10	0.625
15	0.465
20	0.370
25	0.308
35	0.230

Answer

Yes. The plot of $\frac{1}{[A]_t}$ vs. *t* is linear:



Zero-Order Reactions

For zero-order reactions, the differential rate law is:

$$\text{rate} = k$$

A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactant(s). This may seem counterintuitive, since the reaction rate certainly can't be finite when the reactant concentration is zero. For purposes of this introductory text, it will suffice to note that zero-order kinetics are observed for some reactions only under certain specific conditions. These same reactions exhibit different kinetic behaviors when the specific conditions aren't met, and for this reason the more prudent term *pseudo-zero-order* is sometimes used.

The integrated rate law for a zero-order reaction is a linear function:

$$[A]_t = -kt + [A]_0$$
$$y = mx + b$$

A plot of [*A*] versus *t* for a zero-order reaction is a straight line with a slope of $-k$ and a *y*-intercept of $[A]_0$. Figure 12.7.3 shows a plot of [NH_3] versus *t* for the thermal decomposition of ammonia at the surface of two different heated solids. The decomposition reaction exhibits first-order behavior at a quartz (SiO_2) surface, as suggested by the exponentially decaying plot of concentration versus time. On a tungsten surface, however, the plot is linear, indicating zero-order kinetics.

Example 12.7.5: Graphical Determination of Zero-Order Rate Constant

Use the data plot in Figure 12.7.3 to graphically estimate the zero-order rate constant for ammonia decomposition at a tungsten surface.

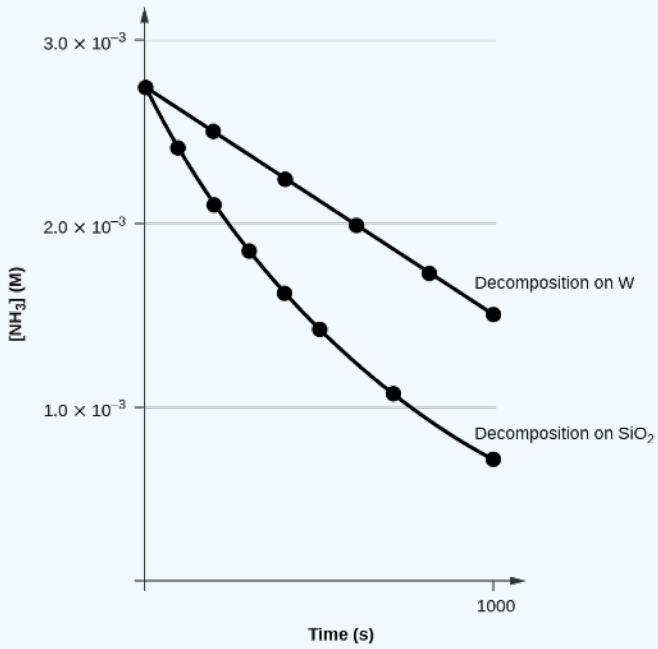


Figure 12.7.3: The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.

Solution

The integrated rate law for zero-order kinetics describes a linear plot of reactant concentration, $[A]_t$, versus time, *t*, with a slope equal to the negative of the rate constant, $-k$. Following the mathematical approach of previous examples, the slope of the linear data plot (for decomposition on W) is estimated from the graph. Using the ammonia concentrations at *t* = 0 and *t* = 1000 s:

$$k = -\text{ slope } = -\frac{\left(0.0015 molL^{-1} - 0.0028 molL^{-1}\right)}{(1000s - 0s)} = 1.3 \times 10^{-6} molL^{-1}s^{-1}$$

Exercise 12.7.5

The zero-order plot in Figure 12.7.3 shows an initial ammonia concentration of 0.0028 mol L^{-1} decreasing linearly with time for 1000 s. Assuming no change in this zero-order behavior, at what time (min) will the concentration reach 0.0001 mol L^{-1}?

Answer

35 min

The Half-Life of a Reaction

The half-life of a reaction ($t_{1/2}$) is the time required for one-half of a given amount of reactant to be consumed. In each succeeding half-life, half of the remaining concentration of the reactant is consumed. Using the decomposition of hydrogen peroxide (Figure 12.7.1) as an example, we find that during the first half-life (from 0.00 hours to 6.00 hours), the concentration of H_2O_2 decreases from 1.000 *M* to 0.500 *M*. During the second half-life (from 6.00 hours to 12.00 hours), it decreases from 0.500 *M* to 0.250 *M*; during the third half-life, it decreases from 0.250 *M* to 0.125 *M*. The concentration of H_2O_2 decreases by half during each successive period of 6.00 hours. The decomposition of hydrogen peroxide is a first-order reaction, and, as can be shown, the half-life of a first-order reaction is independent of the concentration of the reactant. However, half-lives of reactions with other orders depend on the concentrations of the reactants.

First-Order Reactions

An equation relating the half-life of a first-order reaction to its rate constant may be derived from the integrated rate law as follows:

$$\ln \frac{[A]_0}{[A]_t} = kt$$

$$t = \ln \frac{[A]_0}{[A]_t} \times \frac{1}{k}$$

Invoking the definition of half-life, symbolized requires that the concentration of *A* at this point is one-half its initial concentration: $t = t_{1/2}$, $[A]_t = \frac{1}{2}[A]_0$

Substituting these terms into the rearranged integrated rate law and simplifying yields the equation for half-life:

$$t_{1/2} = \ln \frac{[A]_0}{\frac{1}{2}[A]_0} \times \frac{1}{k}$$

$$= \ln 2 \times \frac{1}{k} = 0.693 \times \frac{1}{k}$$

$$t_{1/2} = \frac{0.693}{k}$$

This equation describes an expected inverse relation between the half-life of the reaction and its rate constant, *k*. Faster reactions exhibit larger rate constants and correspondingly shorter half-lives. Slower reactions exhibit smaller rate constants and longer half-lives.

Example 12.7.6: Calculation of a First-order Rate Constant using Half-Life

Calculate the rate constant for the first-order decomposition of hydrogen peroxide in water at 40 °C, using the data given in Figure 12.7.4



Figure 12.7.4: The decomposition of H_2O_2 at 40 °C is illustrated. The intensity of the color symbolizes the concentration of H_2O_2 at the indicated times; H_2O_2 is actually colorless.

Solution

Inspecting the concentration/time data in Figure 12.7.4 shows the half-life for the decomposition of H_2O_2 is 2.16×10^4 s:

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.16 \times 10^4 s} = 3.21 \times 10^{-5} s^{-1}$$

? Exercise 12.7.1

The first-order radioactive decay of iodine-131 exhibits a rate constant of 0.138 d^{-1}. What is the half-life for this decay?

Answer

5.02 d.

Second-Order Reactions

Following the same approach as used for first-order reactions, an equation relating the half-life of a second-order reaction to its rate constant and initial concentration may be derived from its integrated rate law:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

or

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

Restrict t to $t_{1/2}$

$$t = t_{1/2}$$

define $[A]_t$ as one-half $[A]_0$

$$[A]_t = \frac{1}{2}[A]_0$$

and then substitute into the integrated rate law and simplify:

$$\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{1}{[A]_0} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

For a second-order reaction, $t_{1/2}$ is inversely proportional to the concentration of the reactant, and the half-life increases as the reaction proceeds because the concentration of reactant decreases. Unlike with first-order reactions, the rate constant of a second-order reaction cannot be calculated directly from the half-life unless the initial concentration is known.

Zero-Order Reactions

As for other reaction orders, an equation for zero-order half-life may be derived from the integrated rate law:

$$[A] = -kt + [A]_0$$

Restricting the time and concentrations to those defined by half-life: and Substituting these terms into the zero-order integrated rate law yields:

$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

$$kt_{1/2} = \frac{[A]_0}{2}$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

As for all reaction orders, the half-life for a zero-order reaction is inversely proportional to its rate constant. However, the half-life of a zero-order reaction increases as the initial concentration increases.

Equations for both differential and integrated rate laws and the corresponding half-lives for zero-, first-, and second-order reactions are summarized in Table 12.7.1.

Table 12.7.1: Summary of Rate Laws for Zero-, First-, and Second-Order Reactions

	Zero-Order	First-Order	Second-Order
rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
units of rate constant	M s^{-1}	s^{-1}	M^{-1} s^{-1}
integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \left(\frac{1}{[A]_0}\right)$
plot needed for linear fit of rate data	$[A]$ vs. t	ln$[A]$ vs. t	vs. t
relationship between slope of linear plot and rate constant	k = −slope	k = −slope	k = slope
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

Example 12.7.7: Half-Life for Zero-Order and Second-Order Reactions

What is the half-life for the butadiene dimerization reaction described in Example 12.7.3?

Solution

The reaction in question is second order, is initiated with a 0.200 mol L^{-1} reactant solution, and exhibits a rate constant of 0.0576 L mol^{-1} min^{-1}. Substituting these quantities into the second-order half-life equation:

$$t_{1/2} = \frac{1}{\left[\left(0.0576 L mol^{-1} min^{-1}\right)\left(0.200 mol L^{-1}\right)\right]} = 86.8 \text{ min}$$

Exercise 12.7.7

What is the half-life (min) for the thermal decomposition of ammonia on tungsten (see Figure 12.7.3)?

Answer

87 min

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12.8: Collision Theory

Learning Objectives

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

- Use the postulates of collision theory to explain the effects of physical state, temperature, and concentration on reaction rates
- Define the concepts of activation energy and transition state
- Use the Arrhenius equation in calculations relating rate constants to temperature

We should not be surprised that atoms, molecules, or ions must collide before they can react with each other. Atoms must be close together to form chemical bonds. This simple premise is the basis for a very powerful theory that explains many observations regarding chemical kinetics, including factors affecting reaction rates.

Collision theory is based on the following postulates:

1. The rate of a reaction is proportional to the rate of reactant collisions:

$$\text{reaction rate} \propto \frac{\#\ \text{collisions}}{\text{time}}$$

2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

We can see the importance of the two physical factors noted in postulates 2 and 3, the orientation and energy of collisions, when we consider the reaction of carbon monoxide with oxygen:

$$2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$$

Carbon monoxide is a pollutant produced by the combustion of hydrocarbon fuels. To reduce this pollutant, automobiles have catalytic converters that use a catalyst to carry out this reaction. It is also a side reaction of the combustion of gunpowder that results in muzzle flash for many firearms. If carbon monoxide and oxygen are present in sufficient amounts, the reaction will occur at high temperature and pressure.

The first step in the gas-phase reaction between carbon monoxide and oxygen is a collision between the two molecules:

$$CO(g) + O_2(g) \longrightarrow CO_2(g) + O(g)$$

Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in Figure 12.8.1. In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms (\ce{O=C=O}\). This is a rather simple example of how important the orientation of the collision is in terms of creating the desired product of the reaction.

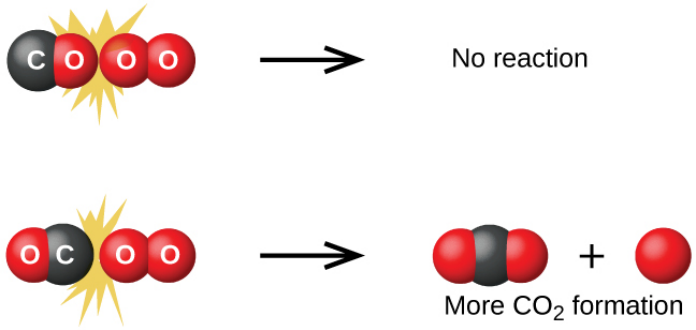


Figure 12.8.1: Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. In addition to a proper orientation, the collision must also occur with sufficient energy to result in product formation. When reactant species collide with both proper orientation and adequate energy, they combine to form an unstable species called an **activated complex** or a **transition state**. These species are very short lived and usually undetectable by most analytical instruments. In some cases, sophisticated spectral measurements have been used to observe transition states.

Collision theory explains why most reaction rates increase as concentrations increase. With an increase in the concentration of any reacting substance, the chances for collisions between molecules are increased because there are more molecules per unit of volume. More collisions mean a faster reaction rate, assuming the energy of the collisions is adequate.

Activation Energy and the Arrhenius Equation

The minimum energy necessary to form a product during a collision between reactants is called the **activation energy** (E_a). How this energy compares to the kinetic energy provided by colliding reactant molecules is a primary factor affecting the rate of a chemical reaction. If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly since only a few fast-moving molecules will have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules, a large fraction of molecules will be adequately energetic and the reaction will proceed rapidly.

Figure $12.8.2$ shows how the energy of a chemical system changes as it undergoes a reaction converting reactants to products according to the equation

$$\mathrm{A^{+}B \longrightarrow C^{+}D}$$

These reaction diagrams are widely used in chemical kinetics to illustrate various properties of the reaction of interest. Viewing the diagram from left to right, the system initially comprises reactants only, $\mathrm{A+B}$. Reactant molecules with sufficient energy can collide to form a high-energy activated complex or transition state. The unstable transition state can then subsequently decay to yield stable products, *C* + *D*. The diagram depicts the reaction's activation energy, E_a, as the energy difference between the reactants and the transition state. Using a specific energy, the *enthalpy* (see chapter on thermochemistry), the enthalpy change of the reaction, ΔH, is estimated as the energy difference between the reactants and products. In this case, the reaction is exothermic ($\Delta H < 0$) since it yields a decrease in system enthalpy.

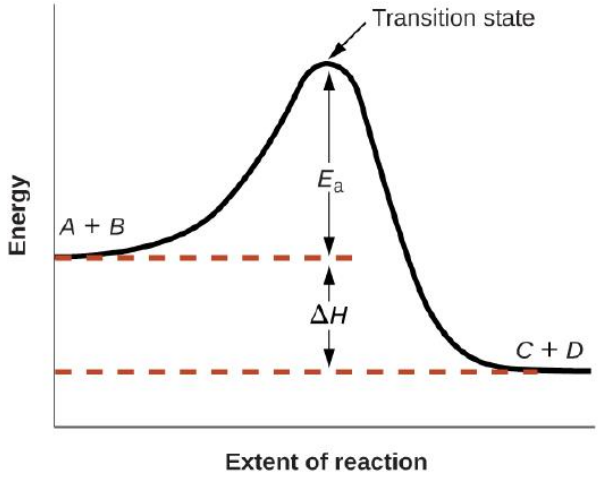


Figure 12.8.2: Reaction diagram for the exothermic reaction

The **Arrhenius equation** relates the activation energy and the rate constant, *k*, for many chemical reactions:

$$k = Ae^{-E_a/RT}$$

In this equation, R is the ideal gas constant, which has a value 8.314 J/mol/K, T is temperature on the Kelvin scale, E_a is the activation energy in joules per mole, *e* is the constant 2.7183, and *A* is a constant called the **frequency factor**, which is related to the frequency of collisions and the orientation of the reacting molecules.

Postulates of collision theory are nicely accommodated by the Arrhenius equation. The frequency factor, *A*, reflects how well the reaction conditions favor properly oriented collisions between reactant molecules. An increased probability of effectively oriented collisions results in larger values for *A* and faster reaction rates.

The exponential term, $e^{-Ea/RT}$, describes the effect of activation energy on reaction rate. According to kinetic molecular theory (see chapter on gases), the temperature of matter is a measure of the average kinetic energy of its constituent atoms or molecules. The distribution of energies among the molecules composing a sample of matter at any given temperature is described by the plot shown in Figure $12.8.3a$. Two shaded areas under the curve represent the numbers of molecules possessing adequate energy (*RT*) to overcome the activation barriers (E_a). A lower activation energy results in a greater fraction of adequately energized molecules and a faster reaction.

The exponential term also describes the effect of temperature on reaction rate. A higher temperature represents a correspondingly greater fraction of molecules possessing sufficient energy (*RT*) to overcome the activation barrier (E_a), as shown in Figure $12.8.3b$ This yields a greater value for the rate constant and a correspondingly faster reaction rate.

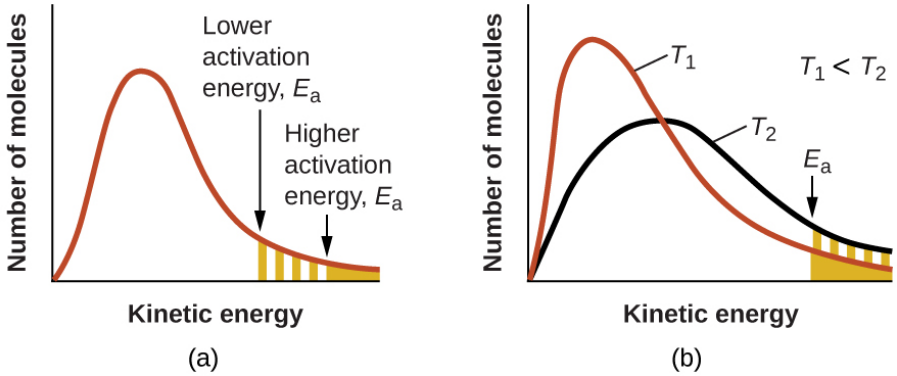


Figure 12.8.3: Molecular energy distributions showing numbers of molecules with energies exceeding (a) two different activation energies at a given temperature, and (b) a given activation energy at two different temperatures.

A convenient approach for determining E_a for a reaction involves the measurement of *k* at two or more different temperatures and using an alternate version of the Arrhenius equation that takes the form of a linear equation

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

$$y = mx + b$$

A plot of $\ln k$ versus $\frac{1}{T}$ is linear with a slope equal to $\frac{-E_a}{R}$ and a y-intercept equal to $\ln A$.

Example 12.8.1: Determination of E_a

The variation of the rate constant with temperature for the decomposition of $HI(g)$ to $H_2(g)$ and $I_2(g)$ is given here. What is the activation energy for the reaction?

$$2\,HI(g) \longrightarrow H_2(g) + I_2(g)$$

T (K)	k (L/mol/s)
555	3.52×10^{-7}
575	1.22×10^{-6}
645	8.59×10^{-5}
700	1.16×10^{-3}
781	3.95×10^{-2}

Solution

Use the provided data to derive values of $\frac{1}{T}$ and $\ln k$:

$\frac{1}{T}$	$\ln k$
1.80×10^{-3}	−14.860
1.74×10^{-3}	−13.617
1.55×10^{-3}	−9.362
1.43×10^{-3}	−6.759
1.28×10^{-3}	−3.231

Figure 12.8.4is a graph of $\ln k$ versus $\frac{1}{T}$. In practice, the equation of the line (slope and *y*-intercept) that best fits these plotted data points would be derived using a statistical process called regression. This is helpful for most experimental data because a perfect fit of each data point with the line is rarely encountered. For the data here, the fit is nearly perfect and the slope may be estimated using any two of the provided data pairs. Using the first and last data points permits estimation of the slope.

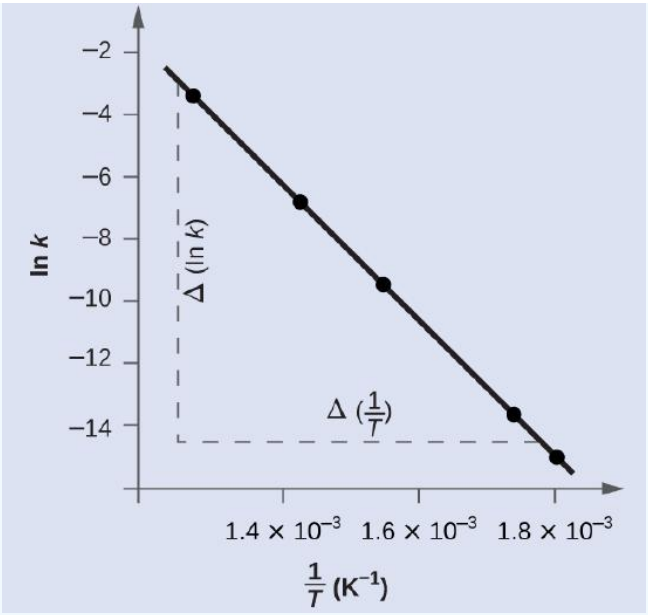


Figure 12.8.4: This graph shows the linear relationship between ln k versus $\frac{1}{T}$ for the reaction $2HI \longrightarrow H_2 + I_2$ according to the Arrhenius equation.

$$\begin{aligned}\text{Slope} &= \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} \\ &= \frac{(-14.860)-(-3.231)}{\left(1.80\times10^{-3}K^{-1}\right)-\left(1.28\times10^{-3}K^{-1}\right)} \\ &= \frac{-11.629}{0.52\times10^{-3}K^{-1}} = -2.2\times10^{4}K \\ &= -\frac{E_a}{R} \\ E_a &= -\text{ slope }\times R = -\left(-2.2\times10^{4}K\times8.314Jmol^{-1}K^{-1}\right) \\ &\quad 1.8\times10^{5}Jmol^{-1} \text{ or } 180kJmol^{-1}\end{aligned}$$

Alternative approach: A more expedient approach involves deriving activation energy from measurements of the rate constant at just two temperatures. In this approach, the Arrhenius equation is rearranged to a convenient two-point form:

$$\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

Rearranging this equation to isolate activation energy yields:

$$E_a = -R\left(\frac{\ln k_2 - \ln k_1}{\left(\frac{1}{T_2}\right)-\left(\frac{1}{T_1}\right)}\right)$$

Any two data pairs may be substituted into this equation—for example, the first and last entries from the above data table:

$$E_a = -8.314Jmol^{-1}K^{-1}\left(\frac{-3.231-(-14.860)}{1.28\times10^{-3}K^{-1}-1.80\times10^{-3}K^{-1}}\right)$$

and the result is E_a = 1.8 10^5 J mol^{-1} or 180 kJ mol^{-1}

This approach yields the same result as the more rigorous graphical approach used above, as expected. In practice, the graphical approach typically provides more reliable results when working with actual experimental data.

Exercise 12.8.1

The rate constant for the rate of decomposition of N_2O_5 to NO and O_2 in the gas phase is 1.66 L/mol/s at 650 K and 7.39 L/mol/s at 700 K:

$$2\,N_2O_5(g) \longrightarrow 4\,NO(g) + 3\,O_2(g)$$

Assuming the kinetics of this reaction are consistent with the Arrhenius equation, calculate the activation energy for this decomposition.

Answer

$1.1\ 10^5$ J mol^{-1} or 110 kJ mol^{-1}

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12.9: Reaction Mechanisms

Learning Objectives

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

- Distinguish net reactions from elementary reactions (steps)
- Identify the molecularity of elementary reactions
- Write a balanced chemical equation for a process given its reaction mechanism
- Derive the rate law consistent with a given reaction mechanism

Chemical reactions very often occur in a step-wise fashion, involving two or more distinct reactions taking place in sequence. A balanced equation indicates what is reacting and what is produced, but it reveals no details about how the reaction actually takes place. The reaction mechanism (or reaction path) provides details regarding the precise, step-by-step process by which a reaction occurs.

The decomposition of ozone, for example, appears to follow a mechanism with two steps:

$$O_3(g) \longrightarrow O_2(g) + O$$
$$O + O_3(g) \longrightarrow 2O_2(g)$$

Each of the steps in a reaction mechanism is an **elementary reaction**. These elementary reactions occur precisely as represented in the step equations, and they must sum to yield the balanced chemical equation representing the overall reaction:

$$2O_3(g) \longrightarrow 3O_2(g)$$

Notice that the oxygen atom produced in the first step of this mechanism is consumed in the second step and therefore does not appear as a product in the overall reaction. Species that are produced in one step and consumed in a subsequent step are called intermediates.

While the overall reaction equation for the decomposition of ozone indicates that two molecules of ozone react to give three molecules of oxygen, the mechanism of the reaction *does not involve the direct collision and reaction of two ozone molecules*. Instead, one O_3 decomposes to yield O_2 and an oxygen atom, and a second O_3 molecule subsequently reacts with the oxygen atom to yield two additional O_2 molecules.

Unlike balanced equations representing an overall reaction, the equations for elementary reactions are explicit representations of the chemical change taking place. The reactant(s) in an elementary reaction's equation undergo only the bond-breaking and/or making events depicted to yield the product(s). For this reason, *the rate law for an elementary reaction may be derived directly from the balanced chemical equation describing the reaction*. This is not the case for typical chemical reactions, for which rate laws may be reliably determined only via experimentation.

Unimolecular Elementary Reactions

The molecularity of an elementary reaction is the number of reactant species (atoms, molecules, or ions). For example, a unimolecular reaction involves the reaction of a *single* reactant species to produce one or more molecules of product:

$$A \longrightarrow \text{ products}$$

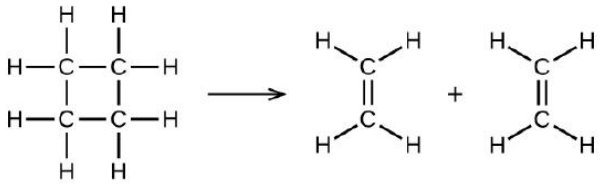
The rate law for a unimolecular reaction is first order:

$$\text{rate } = k[A]$$

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

$$O_3 \longrightarrow O_2 + O$$

illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism as described above. However, some unimolecular reactions may be the only step of a single-step reaction mechanism. (In other words, an "overall" reaction may also be an elementary reaction in some cases.) For example, the gas-phase decomposition of cyclobutane, C_4H_8, to ethylene, C_2H_4, is represented by the following chemical equation:



This equation represents the overall reaction observed, and it might also represent a legitimate unimolecular elementary reaction. The rate law predicted from this equation, assuming it is an elementary reaction, turns out to be the same as the rate law derived experimentally for the overall reaction, namely, one showing first-order behavior:

$$\text{rate } = -\frac{\Delta\left[C_4H_8\right]}{\Delta t} = k\left[C_4H_8\right]$$

This agreement between observed and predicted rate laws is interpreted to mean that the proposed unimolecular, single-step process is a reasonable mechanism for the butadiene reaction.

Bimolecular Elementary Reactions

A bimolecular reaction involves two reactant species, for example:

$$A + B \longrightarrow \text{ products}$$

and

$$2A \longrightarrow \text{ products}$$

For the first type, in which the two reactant molecules are different, the rate law is first-order in *A* and first order in *B* (second-order overall):

$$\text{rate } = k[A][B]$$

For the second type, in which two identical molecules collide and react, the rate law is second order in *A*:

$$\text{rate } = k[A][A] = k[A]^2$$

Some chemical reactions occur by mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

(see Figure 12.9.1)



Figure 12.9.1: The probable mechanism for the reaction between NO_2 and CO to yield NO and CO_2.

Bimolecular elementary reactions may also be involved as steps in a multistep reaction mechanism. The reaction of atomic oxygen with ozone is the second step of the two-step ozone decomposition mechanism discussed earlier in this section:

$$O(g) + O_3(g) \longrightarrow 2O_2(g)$$

Termolecular Elementary Reactions

An elementary termolecular reaction involves the simultaneous collision of three atoms, molecules, or ions. Termolecular elementary reactions are uncommon because the probability of three particles colliding simultaneously is less than one one-thousandth of the probability of two particles colliding. There are, however, a few established termolecular elementary reactions. The reaction of nitric oxide with oxygen appears to involve termolecular steps:

$$2NO + O_2 \longrightarrow 2NO_2$$

$$\text{rate } = k[NO]^2\,[O_2]$$

Likewise, the reaction of nitric oxide with chlorine appears to involve termolecular steps:

$$2NO + Cl_2 \longrightarrow 2NOCl$$

$$\text{rate } = k[NO]^2\,[Cl_2]$$

Relating Reaction Mechanisms to Rate Laws

It's often the case that one step in a multistep reaction mechanism is significantly slower than the others. Because a reaction cannot proceed faster than its slowest step, this step will limit the rate at which the overall reaction occurs. The slowest step is therefore called the rate-limiting step (or rate-determining step) of the reaction Figure 12.9.2



Figure 12.9.2: A cattle chute is a nonchemical example of a rate-determining step. Cattle can only be moved from one holding pen to another as quickly as one animal can make its way through the chute. (credit: Loren Kerns)

As described earlier, rate laws may be derived directly from the chemical equations for elementary reactions. This is not the case, however, for ordinary chemical reactions. The balanced equations most often encountered represent the overall change for some chemical system, and very often this is the result of some multistep reaction mechanisms. In every case, the rate law must be determined from experimental data and the reaction mechanism subsequently deduced from the rate law (and sometimes from other data). The reaction of NO_2 and CO provides an illustrative example:

$$NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$$

For temperatures above 225 °C, the rate law has been found to be:

$$\text{rate } = k\,[NO_2]\,[CO]$$

The reaction is first order with respect to NO_2 and first-order with respect to CO. This is consistent with a single-step bimolecular mechanism and it is *possible* that this is the mechanism for this reaction at high temperatures.

At temperatures below 225 °C, the reaction is described by a rate law that is second order with respect to NO_2:

$$\text{rate } = k[NO_2]^2$$

This rate law is not consistent with the single-step mechanism, but is consistent with the following two-step mechanism:

$$NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g)\ (\text{slow})$$

$$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)\ (\text{fast})$$

The rate-determining (slower) step gives a rate law showing second-order dependence on the NO_2 concentration, and the sum of the two equations gives the net overall reaction.

In general, when the rate-determining (slower) step is the first step in a mechanism, the rate law for the overall reaction is the same as the rate law for this step. However, when the rate-determining step is preceded by a step involving a rapidly reversible reaction the rate law for the overall reaction may be more difficult to derive.

As discussed in several chapters of this text, a reversible reaction is at *equilibrium* when the rates of the forward and reverse processes are equal. Consider the reversible elementary reaction in which NO dimerizes to yield an intermediate species N_2O_2.

$$NO + NO \rightleftharpoons N_2O_2$$

When this reaction is at equilibrium:

$$\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$$
$$k_1[NO]^2 = k_{-1}\,[N_2O_2]$$

This expression may be rearranged to express the concentration of the intermediate in terms of the reactant NO:

$$\left(\frac{k_1[NO]^2}{k_{-1}}\right) = [N_2O_2]$$

Since intermediate species concentrations are not used in formulating rate laws for overall reactions, this approach is sometimes necessary, as illustrated in the following example exercise.

Example 12.9.1: Deriving a Rate Law from a Reaction Mechanism

The two-step mechanism below has been proposed for a reaction between nitrogen monoxide and molecular chlorine:

$$\text{Step 1:} \quad \mathrm{NO(g) + Cl_2(g) \rightleftharpoons NOCl_2(g)} \qquad \text{(fast)}$$
$$\text{Step 2:} \quad \mathrm{NOCl_2(g) + NO(g) \rightleftharpoons 2\,NOCl(g)} \qquad \text{(slow)}$$

Use this mechanism to derive the equation and predicted rate law for the overall reaction.

Solution

The equation for the overall reaction is obtained by adding the two elementary reactions:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

To derive a rate law from this mechanism, first write rates laws for each of the two steps.

$$\text{rate}_{\,1} = k_1[NO]\,[Cl_2] \text{ for the forward reaction of step 1}$$
$$\text{rate}_{\,-1} = k_{-1}\,[NOCl_2] \text{ for the reverse reaction of step 1}$$
$$\text{rate}_{\,2} = k_2\,[NOCl_2]\,[NO] \text{ for step 2}$$

Step 2 is the rate-determining step, and so the rate law for the overall reaction should be the same as for this step. However, the step 2 rate law, as written, contains an intermediate species concentration, [$NOCl_2$]. To remedy this, use the first step's rate laws to derive an expression for the intermediate concentration in terms of the reactant concentrations.

Assuming step 1 is at equilibrium:

$$\text{rate}_{\,1} = \text{rate}_{\,-1}$$
$$k_1[NO]\,[Cl_2] = k_{-1}\,[NOCl_2]$$
$$[NOCl_2] = \left(\frac{k_1}{k_{-1}}\right)[NO]\,[Cl_2]$$

Substituting this expression into the rate law for step 2 yields:

$$\text{rate}_{\,2} = \text{rate}_{\,\text{overall}} = \left(\frac{k_2k_1}{k_{-1}}\right)[NO]^2\,[Cl_2]$$

Exercise 12.9.1

The first step of a proposed multistep mechanism is:

$$\boxed{\ce{F2(g) <=> 2 F(g) \tag{fast}}}$$

Derive the equation relating atomic fluorine concentration to molecular fluorine concentration.

Answer

$$[\mathrm{F}] = \left(\frac{k_1 \left[F_2 \right]}{k_{-1}} \right)^{1/2}$$

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12.10: Catalysis

Learning Objectives

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

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

Among the factors affecting chemical reaction rates discussed earlier in this chapter was the presence of a *catalyst*, a substance that can increase the reaction rate without being consumed in the reaction. The concepts introduced in the previous section on reaction mechanisms provide the basis for understanding how catalysts are able to accomplish this very important function.

Figure 12.10.1 shows reaction diagrams for a chemical process in the absence and presence of a catalyst. Inspection of the diagrams reveals several traits of these reactions. Consistent with the fact that the two diagrams represent the same overall reaction, both curves begin and end at the same energies (in this case, because products are more energetic than reactants, the reaction is endothermic). The reaction mechanisms, however, are clearly different. The uncatalyzed reaction proceeds via a one-step mechanism (one transition state observed), whereas the catalyzed reaction follows a two-step mechanism (two transition states observed) with *a notably lesser activation energy*. This difference illustrates the means by which a catalyst functions to accelerate reactions, namely, by providing an alternative reaction mechanism with a lower activation energy. Although the catalyzed reaction mechanism for a reaction needn't necessarily involve a different number of steps than the uncatalyzed mechanism, it must provide a reaction path whose rate determining step is faster (lower E_a).

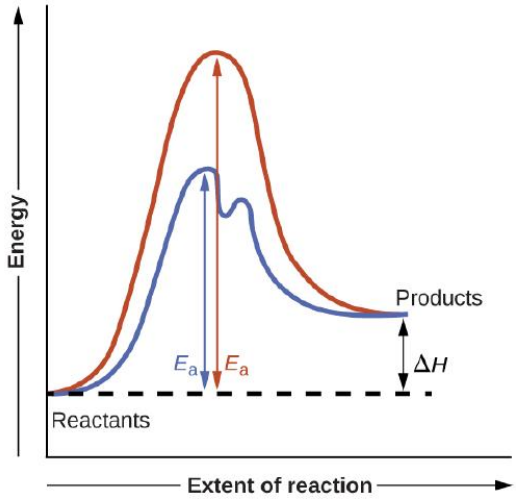
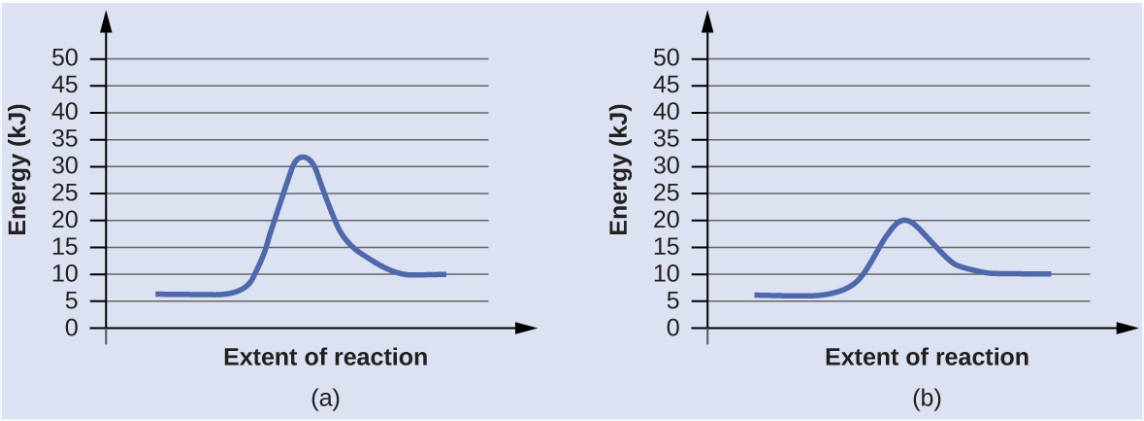


Figure 12.10.1: Reaction diagrams for an endothermic process in the absence (red curve) and presence (blue curve) of a catalyst. The catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

Example 12.10.1: Reaction Diagrams for Catalyzed Reactions

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Estimate the activation energy for each process, and identify which one involves a catalyst.



Solution

Activation energies are calculated by subtracting the reactant energy from the transition state energy.

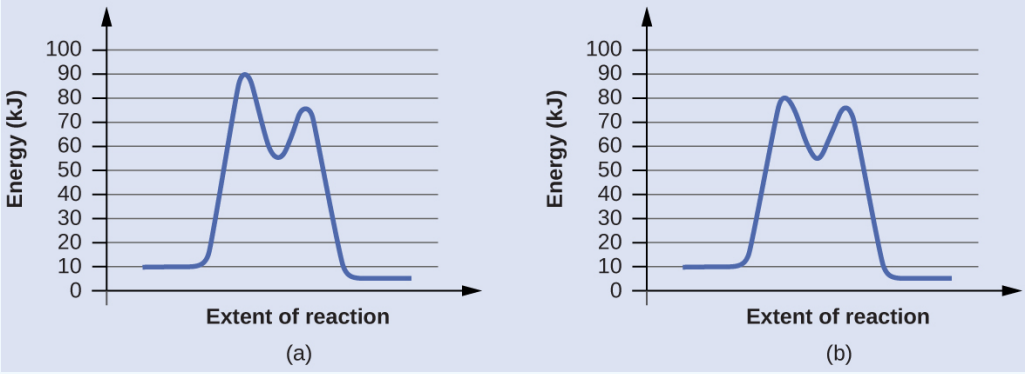
$$\text{diagram}(a): E_a = 32kJ - 6kJ = 26kJ$$

$$\text{diagram}(b): E_a = 20kJ - 6kJ = 14kJ$$

The catalyzed reaction is the one with lesser activation energy, in this case represented by diagram b.

? Exercise 12.10.1

Reaction diagrams for a chemical process with and without a catalyst are shown below. Both reactions involve a two-step mechanism with a rate-determining first step. Compute activation energies for the first step of each mechanism, and identify which corresponds to the catalyzed reaction. How do the second steps of these two mechanisms compare?



Answer

For the first step, E_a = 80 kJ for (a) and 70 kJ for (b), so diagram (b) depicts the catalyzed reaction. Activation energies for the second steps of both mechanisms are the same, 20 kJ.

Homogeneous Catalysts

A homogeneous catalyst is present in the same phase as the reactants. It interacts with a reactant to form an intermediate substance, which then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form product.

As an important illustration of homogeneous catalysis, consider the earth's ozone layer. Ozone in the upper atmosphere, which protects the earth from ultraviolet radiation, is formed when oxygen molecules absorb ultraviolet light and undergo the reaction:

$$3O_2(g) \xrightarrow{h\nu} 2O_3(g)$$

Ozone is a relatively unstable molecule that decomposes to yield diatomic oxygen by the reverse of this equation. This decomposition reaction is consistent with the following two-step mechanism:

$$O_3 \longrightarrow O_2 + O$$
$$O + O_3 \longrightarrow 2O_2$$

A number of substances can catalyze the decomposition of ozone. For example, the nitric oxide–catalyzed decomposition of ozone is believed to occur via the following three-step mechanism:

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$
$$O_3(g) \longrightarrow O_2(g) + O(g)$$
$$NO_2(g) + O(g) \longrightarrow NO(g) + O_2(g)$$

As required, the overall reaction is the same for both the two-step uncatalyzed mechanism and the three-step NO-catalyzed mechanism:

$$2O_3(g) \longrightarrow 3O_2(g)$$

Notice that NO is a reactant in the first step of the mechanism and a product in the last step. This is another characteristic trait of a catalyst: Though it participates in the chemical reaction, it is not consumed by the reaction.

Portrait of a Chemist: Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina (Figure 12.10.2), and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone."[1] Molina's initial discovery of stratospheric depletion of ozone by chlorine atoms was done at the University of California Irvine, he later moved to the NASA/Jet Propulsion Laboratory, MIT and the University of California, San Diego. At the time of his death in 2020 Molina, a Mexican citizen had established a new center for the study of energy and the environment in Mexico City.

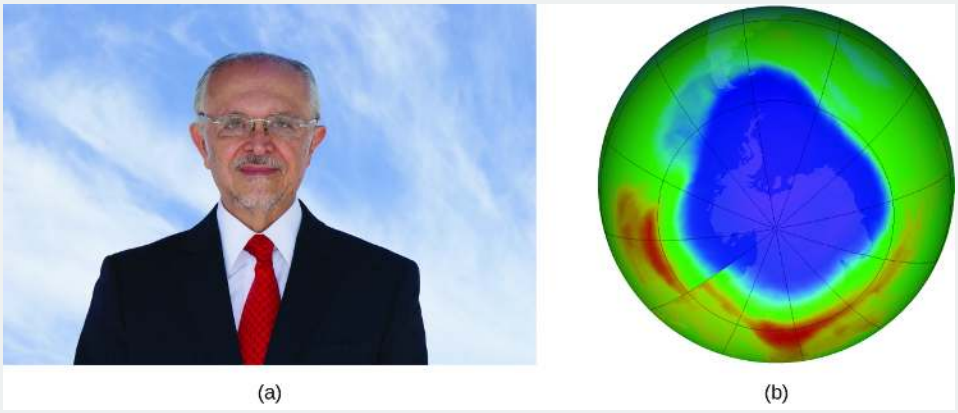


Figure 12.10.2: (a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his (b) early research on stratospheric depletion of ozone and later the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

In 1974, Molina and Rowland published a paper in the journal *Nature* detailing the threat of chlorofluorocarbon gases to the stability of the ozone layer in earth's upper atmosphere. The ozone layer protects earth from solar radiation by absorbing ultraviolet light. As chemical reactions deplete the amount of ozone in the upper atmosphere, a measurable "hole" forms above Antarctica, and an increase in the amount of solar ultraviolet radiation— strongly linked to the prevalence of skin cancers—reaches earth's surface. The work of Molina and Rowland was instrumental in the adoption of the Montreal Protocol, an international treaty signed in 1987 that successfully began phasing out production of chemicals linked to ozone destruction.

Molina and Rowland demonstrated that chlorine atoms from human-made chemicals can catalyze ozone destruction in a process similar to that by which NO accelerates the depletion of ozone. Chlorine atoms are generated when chlorocarbons or chlorofluorocarbons—once widely used as refrigerants and propellants—are photochemically decomposed by ultraviolet light or react with hydroxyl radicals. A sample mechanism is shown here using methyl chloride:

$$CH_3Cl + OH \longrightarrow Cl + \text{ other products} \tag{12.10.1}$$

Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:

$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O \longrightarrow Cl + O_2$$

overall Reaction: $O_3 + O \longrightarrow 2O_2$ \nonumber \]

A single monatomic chlorine can break down thousands of ozone molecules. Luckily, the majority of atmospheric chlorine exists as the catalytically inactive forms Cl_2 and $ClONO_2$.

Enzymes in the human body act as catalysts for important chemical reactions in cellular metabolism. As such, a deficiency of a particular enzyme can translate to a life-threatening disease. G6PD (glucose-6-phosphate dehydrogenase) deficiency, a genetic condition that results in a shortage of the enzyme glucose-6-phosphate dehydrogenase, is the most common enzyme deficiency in humans. This enzyme, shown in Figure 12.21, is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells (Figure 12.10.4).

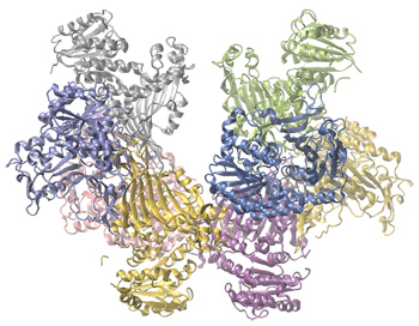


Figure 12.21 Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

A disruption in this pathway can lead to reduced glutathione in red blood cells; once all glutathione is consumed, enzymes and other proteins such as hemoglobin are susceptible to damage. For example, hemoglobin can be metabolized to bilirubin, which leads to jaundice, a condition that can become severe. People who suffer from G6PD deficiency must avoid certain foods and medicines containing chemicals that can trigger damage their glutathione-deficient red blood cells.

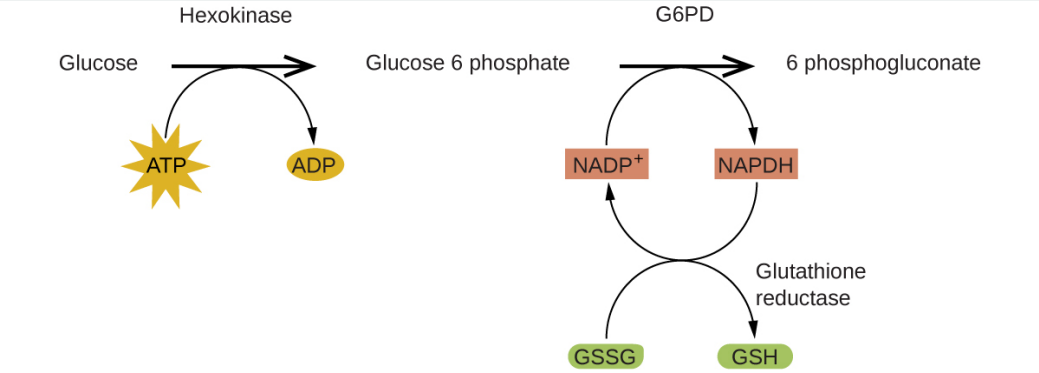


Figure 12.10.4: In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NADPH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

Heterogeneous Catalysts

A heterogeneous catalyst is a catalyst that is present in a different phase (usually a solid) than the reactants. Such catalysts generally function by furnishing an active surface upon which a reaction can occur. Gas and liquid phase reactions catalyzed by heterogeneous catalysts occur on the surface of the catalyst rather than within the gas or liquid phase.

Heterogeneous catalysis typically involves the following processes:

1. Adsorption of the reactant(s) onto the surface of the catalyst
2. Activation of the adsorbed reactant(s)
3. Reaction of the adsorbed reactant(s)

Figure 12.10.5 illustrates the steps of a mechanism for the reaction of compounds containing a carbon–carbon double bond with hydrogen on a nickel catalyst. Nickel is the catalyst used in the hydrogenation of polyunsaturated fats and oils (which contain several carbon–carbon double bonds) to produce saturated fats and oils (which contain only carbon–carbon single bonds).

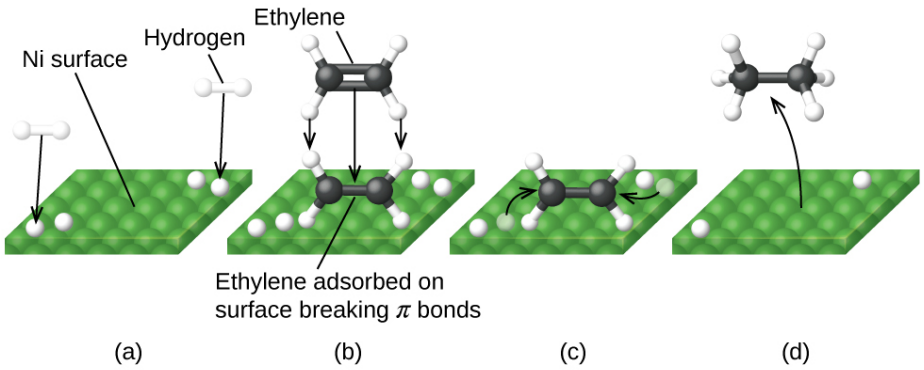


Figure 12.10.5: Mechanism for the Ni-catalyzed reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the C–C π-bond and forming Ni–C bonds. (c) Atoms diffuse across the surface and form new C–H bonds when they collide. (d) C_2H_6 molecules desorb from the Ni surface.

Many important chemical products are prepared via industrial processes that use heterogeneous catalysts, including ammonia, nitric acid, sulfuric acid, and methanol. Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles (Figure 12.10.6).

Chemistry in Everyday Life: Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. By utilizing a carefully selected blend of catalytically active metals, it is possible to effect complete combustion of all carbon-containing compounds to carbon dioxide while also reducing the output of nitrogen oxides. This is particularly impressive when we consider that one step involves adding more oxygen to the molecule and the other involves removing the oxygen (Figure 12.10.6).

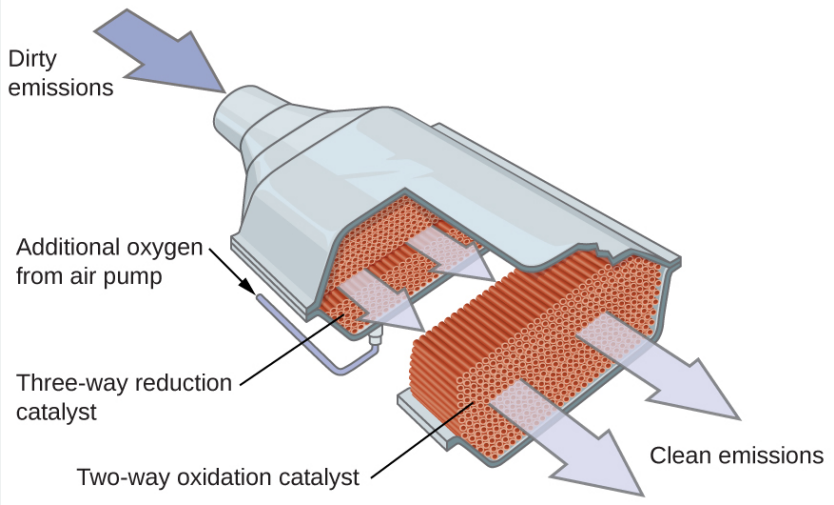


Figure 12.10.6: A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion of nitric oxide into dinitrogen and oxygen as well as the conversion of carbon monoxide and hydrocarbons such

as octane into carbon dioxide and water vapor:

$$2NO_2(g) \longrightarrow N_2(g) + 2O_2(g)$$
$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$
$$2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

In order to be as efficient as possible, most catalytic converters are preheated by an electric heater. This ensures that the metals in the catalyst are fully active even before the automobile exhaust is hot enough to maintain appropriate reaction temperatures.

Link to Learning

The LibreTexts provides a thorough explanation of how catalytic converters work.

How Sciences Interconnect: Enzyme Structure and Function

The study of enzymes is an important interconnection between biology and chemistry. Enzymes are usually proteins (polypeptides) that help to control the rate of chemical reactions between biologically important compounds, particularly those that are involved in cellular metabolism. Different classes of enzymes perform a variety of functions, as shown in Table 12.10.1.

Table 12.10.1: Classes of Enzymes and Their Functions

Class	Function
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Enzyme molecules possess an active site, a part of the molecule with a shape that allows it to bond to a specific substrate (a reactant molecule), forming an enzyme-substrate complex as a reaction intermediate. There are two models that attempt to explain how this active site works. The most simplistic model is referred to as the lock-and-key hypothesis, which suggests that the molecular shapes of the active site and substrate are complementary, fitting together like a key in a lock. The induced fit hypothesis, on the other hand, suggests that the enzyme molecule is flexible and changes shape to accommodate a bond with the substrate. This is not to suggest that an enzyme's active site is completely malleable, however. Both the lock-and-key model and the induced fit model account for the fact that enzymes can only bind with specific substrates, since in general a particular enzyme only catalyzes a particular reaction (Figure 12.10.7).

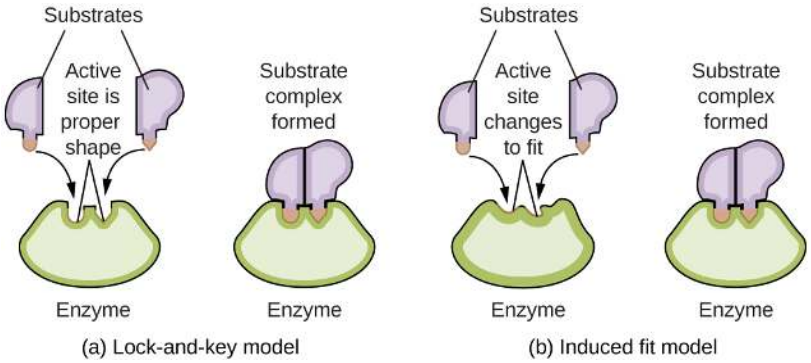


Figure 12.10.7: (a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

Link to Learning

The Royal Society of Chemistry provides an excellent introduction to enzymes for students and teachers.

Footnotes

- 1"The Nobel Prize in Chemistry 1995," Nobel Prize.org, accessed February 18, 2015, http://www.nobelprize.org/nobel_priz...aureates/1995/.

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12.11: Key Terms

activated complex | (also, transition state) unstable combination of reactant species formed during a chemical reaction

activation energy (E_a) | minimum energy necessary in order for a reaction to take place

Arrhenius equation | mathematical relationship between a reaction's rate constant, activation energy, and temperature

average rate | rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred

bimolecular reaction | elementary reaction involving two reactant species

catalyst | substance that increases the rate of a reaction without itself being consumed by the reaction

collision theory | model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics

elementary reaction | reaction that takes place in a single step, precisely as depicted in its chemical equation

frequency factor (A) | proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation

half-life of a reaction ($t_{1/2}$) | time required for half of a given amount of reactant to be consumed

heterogeneous catalyst | catalyst present in a different phase from the reactants, furnishing a surface at which a reaction can occur

homogeneous catalyst | catalyst present in the same phase as the reactants

initial rate | instantaneous rate of a chemical reaction at $t = 0$ s (immediately after the reaction has begun)

instantaneous rate | rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time

integrated rate law | equation that relates the concentration of a reactant to elapsed time of reaction

intermediate | species produced in one step of a reaction mechanism and consumed in a subsequent step

method of initial rates | common experimental approach to determining rate laws that involves measuring reaction rates at varying initial reactant concentrations

molecularity | number of reactant species involved in an elementary reaction

overall reaction order | sum of the reaction orders for each substance represented in the rate law

rate constant (k) | proportionality constant in a rate law

rate expression | mathematical representation defining reaction rate as change in amount, concentration, or pressure of reactant or product species per unit time

rate law | (also, rate equation) (also, differential rate laws) mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants

rate of reaction | measure of the speed at which a chemical reaction takes place

rate-determining step | (also, rate-limiting step) slowest elementary reaction in a reaction mechanism; determines the rate of the overall reaction

reaction diagram | used in chemical kinetics to illustrate various properties of a reaction

reaction mechanism | stepwise sequence of elementary reactions by which a chemical change takes place

reaction order | value of an exponent in a rate law (for example, zero order for 0, first order for 1, second order for 2, and so on)

termolecular reaction | elementary reaction involving three reactant species

unimolecular reaction | elementary reaction involving a single reactant species

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12.12: Key Equations

integrated rate law for zero-order reactions:
half-life for a zero-order reaction
integrated rate law for first-order reactions:
half-life for a first-order reaction
integrated rate law for second-order reactions:
half-life for a second-order reaction

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CHAPTER OVERVIEW

13: Chemical Equilibrium

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

Template:HideTOC

Chemical equilibrium is the state in which both reactants and products are present in concentrations which have no further tendency to change with time. This results when the forward reaction proceeds at the same rate as the reverse reaction. Thus, no net changes in the concentrations of the reactant(s) and product(s) are observed. This is known as dynamic equilibrium.

13.1: The Nature of Chemical Equilibrium
13.2: The Empirical Law of Mass Action
13.3: Thermodynamic Description of the Equilibrium State
13.4: The Law of Mass Action for Related and Simultaneous Equilibria
13.5: Equilibrium Calculations for Gas-Phase and Heterogenous Reactions
13.6: Reaction Directions (Empirical Explanation)
13.7: Reaction Directions (Thermodynamic Explanation)
13.8: Distribution of a Single Species between Immiscible Phases - Extraction and Separation
13.E: Chemical Equilibria (Exercises)

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13.1: 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 13.1.1: 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 13.1.1). The reaction can be followed visually because the product (NO_2) is colored, whereas the reactant (N_2O_4) is colorless:

$$\underset{colorless}{N_2O_4(g)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \underset{red-brown}{2\,NO_2(g)} \tag{13.1.1}$$

The double arrow indicates that both the forward reaction

$$N_2O_4(g) \xrightarrow{k_f} 2\,NO_2(g) \tag{13.1.2}$$

and reverse reaction

$$2\,NO_2(g) \xrightarrow{k_r} N_2O_4(g) \tag{13.1.3}$$

occurring simultaneously (i.e, the reaction is reversible). However, this does not necessarily mean the system is equilibrium as the following chapter demonstrates.

Figure 13.1.2 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 13.1.2*a*), in accordance with the

stoichiometry of the reaction, we reach exactly the same equilibrium composition (Figure 13.1.2*b*). Thus equilibrium can be approached from either direction in a chemical reaction.

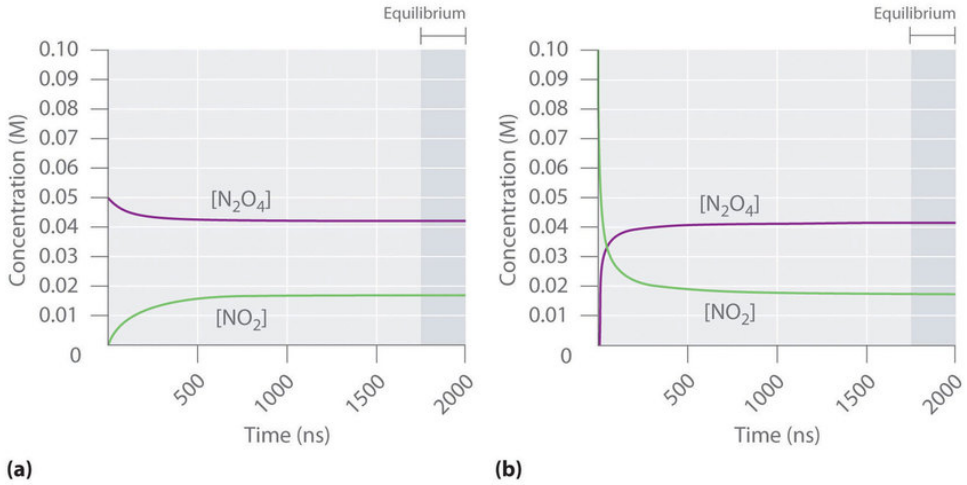


Figure 13.1.2: The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system 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 13.1.3 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 13.1.1 and 13.1.2). Eventually, the forward and reverse reaction rates become identical, $k_f = k_r$, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at different rates, then the system is not at equilibrium.

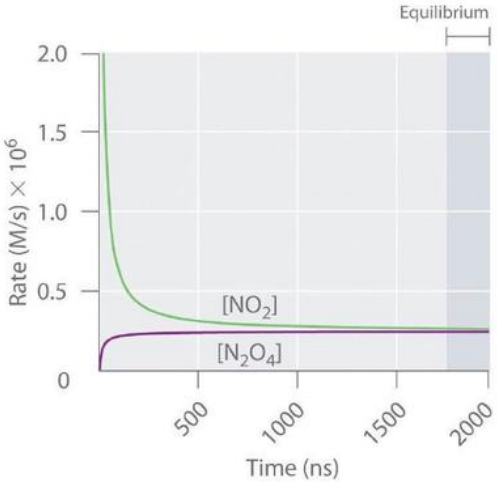


Figure 13.1.3: The Forward and Reverse Reaction Rates as a Function of Time for the $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ System Shown in Part (b) in Figure 13.1.2. (CC BY-SA-NC; Anonymous by request)

The rate of dimerization of NO_2 (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of N_2O_4 is zero, the rate of the dissociation reaction (forward reaction) at $t = 0$ is also zero. As the dimerization reaction proceeds, the N_2O_4 concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of N_2O_4 and NO_2 no longer change.

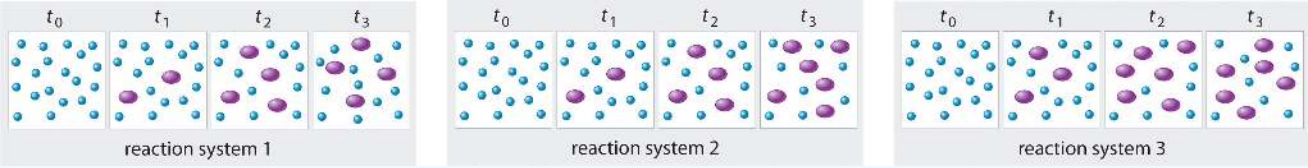
> *At equilibrium, the forward reaction rate is equal to the reverse reaction rate.*

Example 13.1.1

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:

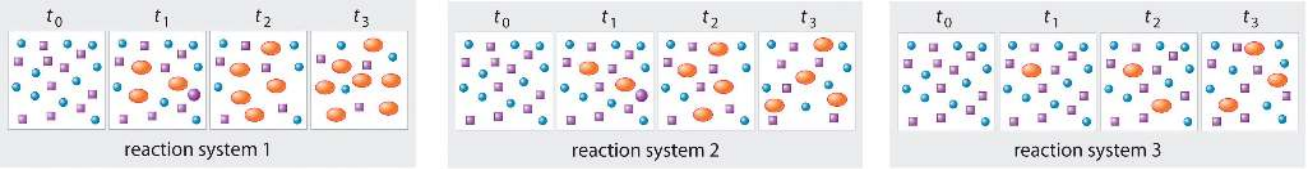
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

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 13.1.1

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B ⇌ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?



In reaction system 1 there are seven orange ovals at t3. In reaction system two there are four orange ovals at t3. In reaction system three there are three orange ovals at t3.

Answer

system 2



A Video Introduction to Dynamic Equilibrium: Introduction to Dynamic Equilibrium(opens in new window) [youtu.be]

Summary

At equilibrium, the forward and reverse reactions of a system proceed at equal rates. Chemical equilibrium is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

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13.2: The Empirical Law of Mass Action

Learning Objectives

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.
- To understand how different phases affect equilibria.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the decomposition reaction of N_2O_4 to NO_2. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[\mathrm{N_2O_4}] \tag{13.2.1}$$

and

$$\text{reverse rate} = k_r[\mathrm{NO_2}]^2 \tag{13.2.2}$$

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

$$k_f[\mathrm{N_2O_4}] = k_r[\mathrm{NO_2}]^2 \tag{13.2.3}$$

so

$$\frac{k_f}{k_r} = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]} \tag{13.2.4}$$

The ratio of the rate constants gives us a new constant, the **equilibrium constant** (K), which is defined as follows:

$$K = \frac{k_f}{k_r} \tag{13.2.5}$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.

> The equilibrium constant is equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction.

Table 13.2.1 lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 13.2.1. 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 NO_2 and 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 13.2.5). That is, at a given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of the reactants and products vary depending on their initial concentrations.

Table 13.2.1: Initial and Equilibrium Concentrations for $NO_2 : N_2O_4$ Mixtures at 25°C

	Initial Concentrations		Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
1	0.0500	0.0000	0.0417	0.0165	6.54×10^{-3}
2	0.0000	0.1000	0.0417	0.0165	6.54×10^{-3}
3	0.0750	0.0000	0.0647	0.0206	6.56×10^{-3}
4	0.0000	0.0750	0.0304	0.0141	6.54×10^{-3}

	Initial Concentrations		Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
5	0.0250	0.0750	0.0532	0.0186	6.50×10^{-3}

Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction of the general form

$$aA + bB \rightleftharpoons cC + dD \tag{13.2.6}$$

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{13.2.7}$$

where K is the equilibrium constant for the reaction. Equation 13.2.6 is called the equilibrium equation, and the right side of Equation 13.2.7 is called the equilibrium constant expression. The relationship shown in Equation 13.2.7 is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of K shown in Table 13.2.2, 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 13.2.2: Equilibrium Constants for Selected Reactions*

Reaction	Temperature (K)	Equilibrium Constant (K)
$S(s) + O_2(g) \rightleftharpoons SO_2(g)$	300	4.4×10^{53}
$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g)$	500	2.4×10^{47}
$H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g)$	300	1.6×10^{33}
$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$	300	4.1×10^{18}
$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$	300	4.2×10^{13}
$3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$	300	2.7×10^{8}
$H_2(g) + D_2(g) \rightleftharpoons 2\,HD(g)$	100	1.92
$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$	300	2.9×10^{-1}
$I_2(g) \rightleftharpoons 2\,I(g)$	800	4.6×10^{-7}
$Br_2(g) \rightleftharpoons 2\,Br(g)$	1000	4.0×10^{-7}
$Cl_2(g) \rightleftharpoons 2\,Cl(g)$	1000	1.8×10^{-9}
$F_2(g) \rightleftharpoons 2\,F(g)$	500	7.4×10^{-13}

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.

You will also notice in Table 13.2.2 that equilibrium constants have no units, even though Equation 13.2.7 suggests that the units of concentration might not always cancel because the exponents may vary. **In fact, equilibrium constants are calculated using "effective concentrations," or activities, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M.** As shown in Equation 13.2.8, the units of concentration cancel, which makes K unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{mol}{\cancel{L}}}{\frac{mol}{\cancel{L}}} \tag{13.2.8}$$

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

$$\mathrm{H_2(g) + D_2(g) \rightleftharpoons 2\,HD(g)} \tag{13.2.9}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]} \tag{13.2.10}$$

with K varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of $\mathrm{H_2}$, $\mathrm{D_2}$, and HD contains significant concentrations of both product and reactants.

Figure 13.2.1 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 13.2.8 and 13.2.7), when $k_f \gg k_r$, K is a **large** number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f \ll k_r$, K is a very **small** number, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium.

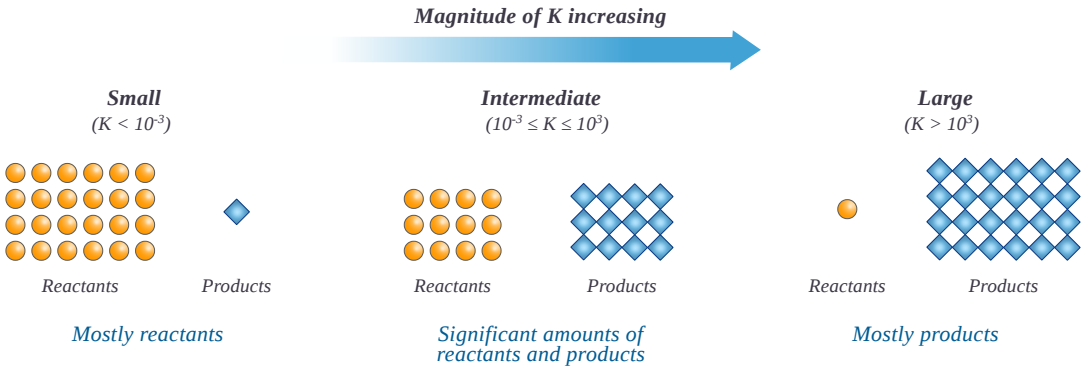


Figure 13.2.1: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium. (CC BY-NC; 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 13.2.1

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 13.2.7. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

The only product is ammonia, which has a coefficient of 2. For the reactants, N_2 has a coefficient of 1 and $\mathrm{H_2}$ 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 13.2.1

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 13.2.2

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 13.2.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

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

Values of the equilibrium constant at various temperatures were reported as

- $K_{25^\circ C} = 3.3 \times 10^8$,
- $K_{177^\circ C} = 2.6 \times 10^3$, and
- $K_{327^\circ C} = 4.1$.

a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
b. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer a

327°C, where K is smallest

Answer b

25°C

Variations in the Form of the Equilibrium Constant Expression

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 13.2.6 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{13.2.11}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \tag{13.2.12}$$

This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is as follows:

$$K = \frac{[NO_2]^2}{[N_2O_4]} \tag{13.2.13}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K′ is given by the inverse expression:

$$K' = \frac{[N_2O_4]}{[NO_2]^2} \tag{13.2.14}$$

Consider another example, the formation of water: $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$. Because H_2 is a good reductant and O_2 is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form O_2 and H_2, is very small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into H_2 and O_2.

> The equilibrium constant for a reaction written in reverse is the *inverse* of the equilibrium constant for the reaction as written originally.

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, we could write the equation for the reaction

$$2NO_2 \rightleftharpoons N_2O_4 \tag{13.2.15}$$

as

$$NO_2 \rightleftharpoons \frac{1}{2}N_2O_4 \tag{13.2.16}$$

with the equilibrium constant K″ is as follows:

$$K'' = \frac{[N_2O_4]^{1/2}}{[NO_2]} \tag{13.2.17}$$

The values for K′ (Equation 13.2.14) and K″ are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{13.2.18}$$

In general, if all the coefficients in a balanced chemical equation were subsequently multiplied by n, then the new equilibrium constant is the original equilibrium constant raised to the nth power.

Example 13.2.3: The Haber Process

At 745 K, K is 0.118 for the following reaction:

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)}$$

What is the equilibrium constant for each related reaction at 745 K?

a. $\mathrm{2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)}$
b. $\mathrm{\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)}$

Given: balanced equilibrium equation, K at a given temperature, and equations of related reactions

Asked for: values of K for related reactions

Strategy:

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate K for each reaction.

Solution:

The equilibrium constant expression for the given reaction of $\mathrm{N_2(g)}$ with $\mathrm{H_2(g)}$ to produce $\mathrm{NH_3(g)}$ at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118$$

This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47$$

In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344$$

? Exercise

At 527°C, the equilibrium constant for the reaction

$$\mathrm{2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)}$$

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$\mathrm{SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g)}$$

Answer

3.6×10^{-3}

Law of Mass Action for Gas-Phase Reactions

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol K_p is used to denote equilibrium constants calculated from partial pressures. For the general reaction

$$\mathrm{aA + bB \rightleftharpoons cC + dD}$$

in which all the components are gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \tag{13.2.19}$$

Thus K_p for the decomposition of N_2O_4 (Equation 13.2.1) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \tag{13.2.20}$$

Like K, K_p is a unitless quantity because the quantity that is actually used to calculate it is an "effective pressure," the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity. The "effective pressure" is called the **fugacity**, just as activity is the effective concentration.

Because partial pressures are usually expressed in atmospheres or mmHg, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, the numerical values of K and K_p are usually different. They are, however, related by the ideal gas constant (R) and the absolute temperature (T):

$$K_p = K(RT)^{\Delta n} \tag{13.2.21}$$

where K is the equilibrium constant expressed in units of concentration and Δn is the difference between the numbers of moles of gaseous products and gaseous reactants ($n_p - n_r$). The temperature is expressed as the absolute temperature in Kelvin. According to Equation 13.2.21, $K_p = K$ only if the moles of gaseous products and gaseous reactants are the same (i.e., $\Delta n = 0$). For the decomposition of N_2O_4, there are 2 mol of gaseous product and 1 mol of gaseous reactant, so $\Delta n = 1$. Thus, for this reaction,

$$K_p = K(RT)^1 = KRT \tag{13.2.22}$$

Example 13.2.4: 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 13.2.21to calculate K from K_p.

Solution:

This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2 - 4) = -2$. We know K, and $T = 745\ K$. Thus, from Equation 13.2.18, we have the following:

$$K_p = K(RT)^{-2} = \frac{K}{(RT)^2} = \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2} = 3.16 \times 10^{-5}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

Exercise 13.2.4:

Calculate K_p for the reaction

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

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer

$K_p = 1.2 \times 10^3$

Law of Mass Action for Reactions Involving Pure Substances and Multiple Phases

When the products and reactants of a reaction at equilibrium in a single phase (e.g., liquid, gas or solids of different lattices), the system is a **homogeneous equilibrium**. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system where the reactants and products are in two or more phase is called a **heterogeneous equilibrium** (e.g, the reaction of a gas with a solid or liquid or two different solid lattices in co-existing).

Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, their concentrations are treated as constants, which allows us to simplify equilibrium constant expressions that involve pure solids or liquids.The reference states for pure solids and liquids are those forms stable at 1 bar (approximately 1 atm), which are assigned an activity of 1. (Recall that the density of water, and thus its volume, changes by only a few percentage points between 0 °C and 100 °C.)

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$\mathrm{CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)} \tag{13.2.23}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{[CO]^2}{[CO_2][C]} \tag{13.2.24}$$

Because graphite is a solid, however, its molar concentration, determined from its density and molar mass, is essentially constant and has the following value:

$$[C] = \frac{2.26\ \cancel{g}/\ \cancel{cm^3}}{12.01\ \cancel{g}/mol} \times 1000\ \ \cancel{cm^3}/L = 188\ mol/L = 188\ M \tag{13.2.25}$$

We can rearrange Equation 13.2.25 so that the constant terms are on one side:

$$K[C] = K(188) = \frac{[CO]^2}{[CO_2]} \tag{13.2.26}$$

Incorporating the constant value of $[C]$ into the equilibrium equation for the reaction in Equation 13.2.26,

$$K' = \frac{[CO]^2}{[CO_2]} \tag{13.2.27}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{13.2.28}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the concentrations of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and CO_2, the system described in Equation 13.2.23 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 13.2.2, 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.

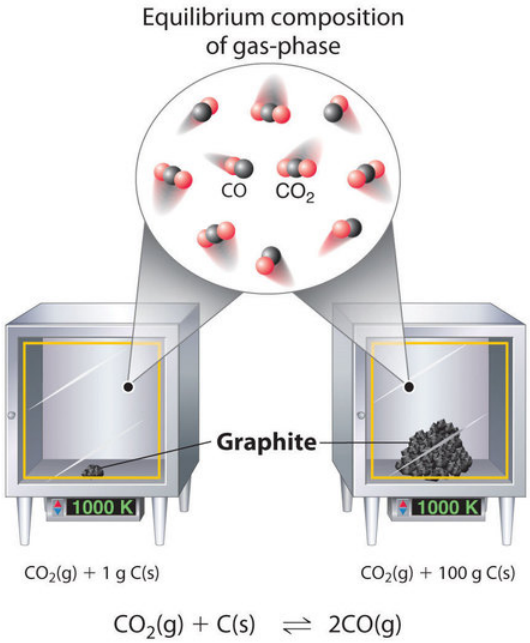


Figure 13.2.2: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

Example 13.2.1

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 13.2.1

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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13.3: Thermodynamic Description of the Equilibrium State

Learning Objectives

- Gibbs Energy is a state function defined as $G = H - TS$.
- The practical utility of the Gibbs function is that ΔG for any process is negative if it leads to an increase in the entropy of the world. Thus spontaneous change at a given temperature and pressure can only occur when it would lead to a decrease in G.
- The sign of the standard free energy change ΔG^o of a chemical reaction determines whether the reaction will tend to proceed in the forward or reverse direction.
- Similarly, the relative signs of ΔH^o and ΔH^o determine whether the spontaneity of a chemical reaction will be affected by the temperature, and if so, in what way.
- The existence of sharp melting and boiling points reflects the differing temperature dependancies of the free energies of the solid, liquid, and vapor phases of a pure substance, which are in turn reflect their differing entropies.

Previously, we saw that it is the **sum** of the entropy changes of the system and surroundings that determines whether a process will occur spontaneously. In chemical thermodynamics we prefer to focus our attention on the system rather than the surroundings, and would like to avoid having to calculate the entropy change of the surroundings explicitly.

In this unit we introduce a new thermodynamic function, the *free energy*, which turns out to be the single most useful criterion for predicting the direction of a chemical reaction and the composition of the system at equilibrium. However, the term "free energy", although still widely used, is rather misleading, so we will often refer to it as "Gibbs energy." The free energy enables us to do this for changes that occur at a constant temperature and pressure (the *Gibbs energy*) or constant temperature and volume (the *Helmholtz energy*.)

Free energy: the Gibbs function

The Gibbs energy (also known as the *Gibbs function* or *Gibbs Potential*) is defined as

$$G = H - TS \tag{13.3.1}$$

in which S refers to the entropy of the *system*. Since H, T and S are all state functions, so is G. Thus for any change in state (under constant temperature), we can write the extremely important relation

$$\Delta G = \Delta H - T\Delta S \tag{13.3.2}$$

How does this simple equation encompass the entropy change of the world ΔS_{total}, which we already know is the sole criterion for spontaneous change from the second law of thermodynamics? Starting with the definition

$$\Delta S_{total} = \Delta S_{surr} + \Delta S_{sys} \tag{13.3.3}$$

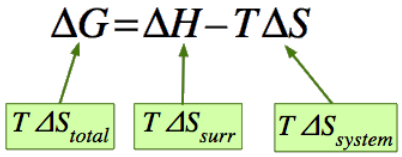
we would first like to get rid of ΔS_{surr}. How can a chemical reaction (a change in the *system*) affect the entropy of the *surroundings*? Because most reactions are either exothermic or endothermic, they are accompanied by a flow of heat q_p across the system boundary. The enthalpy change of the reaction ΔH is defined as the flow of heat into the system from the surroundings when the reaction is carried out at constant pressure, so the heat withdrawn from the surroundings will be $-q_p$ which will cause the entropy of the surroundings to change by $-q_p/T = -\Delta H/T$. We can therefore rewrite Equation 13.3.3 as

$$\Delta S_{total} = \frac{-\Delta H}{T} + \Delta S_{sys} \tag{13.3.4}$$

Multiplying each side by $-T$, we obtain

$$-T\Delta S_{total} = \Delta H - T\Delta S_{sys} \tag{13.3.5}$$

which expresses the entropy change of the world in terms of thermodynamic properties of the *system* exclusively. If $-T\Delta S_{total}$ is denoted by ΔG, then we have Equation 13.3.2 which defines the *Gibbs energy* change for the process.



From the foregoing, you should convince yourself that G will decrease in any process occurring at constant temperature and pressure which is accompanied by an overall increase in the entropy. The constant temperature is a consequence of the temperature and the enthalpy appearing in the preceding Equation 13.3.5. Since most chemical and phase changes of interest to chemists take place under such conditions, the Gibbs energy is the most useful of all the thermodynamic properties of a substance, and (as we shall see in the lesson that follows this one) it is closely linked to the equilibrium constant.

Some textbooks and teachers say that the free energy, and thus the spontaneity of a reaction, depends on both the enthalpy and entropy changes of a reaction, and they sometimes even refer to reactions as "energy driven" or "entropy driven" depending on whether ΔH or the $T\Delta S$ term dominates. This is technically correct, but misleading because it disguises the important fact that ΔS_{total}, which this equation expresses in an indirect way, is the *only* criterion of spontaneous change.

Helmholtz Energy is also a "Free Energy"

We will deal only with the Gibbs energy in this course. The Helmholtz free energy is of interest mainly to chemical engineers (whose industrial-scale processes are often confined to tanks and reactors of fixed volume) and some geochemists whose interest is centered on the chemistry that occurs deep within the earth's surface.

Gibbs Energy and Chemical Change

Remember that ΔG is meaningful only for changes in which the *temperature and pressure remain constant*. These are the conditions under which most reactions are carried out in the laboratory; the system is usually open to the atmosphere (constant pressure) and we begin and end the process at room temperature (after any heat we have added or which is liberated by the reaction has dissipated.) The importance of the Gibbs function can hardly be over-stated: it serves as the single master variable that determines whether a given chemical change is thermodynamically possible. Thus if the free energy of the reactants is greater than that of the products, the entropy of the world will increase when the reaction takes place as written, and so the reaction will tend to take place spontaneously. Conversely, if the free energy of the products exceeds that of the reactants, then the reaction will not take place in the direction written, but it will tend to proceed in the reverse direction.

> *ΔG serves as the single master variable that determines whether a given chemical change is thermodynamically possible. Moreover, it determines the direction and extent of chemical change.*

In a spontaneous change, Gibbs energy always decreases and never increases. This of course reflects the fact that the entropy of the world behaves in the exact opposite way (owing to the negative sign in the $T\Delta S$ term).

$$\mathrm{H_2O(l) \rightarrow H_2O(s)} \tag{13.3.6}$$

water below its freezing point undergoes a decrease in its entropy, but the heat released into the surroundings more than compensates for this, so the entropy of the world increases, the free energy of the H_2O diminishes, and the process proceeds spontaneously.

> *In a spontaneous change, Gibbs energy **always** decreases and never increases.*

An important consequence of the one-way downward path of the free energy is that once it reaches its minimum possible value, all net change comes to a halt. This, of course, represents the state of chemical equilibrium. These relations are nicely summarized as follows:

- $\Delta G < 0$: reaction can spontaneously proceed to the right:

$$A \rightarrow B$$

- $\Delta G > 0$: reaction can spontaneously proceed to the left:

$$A \leftarrow B$$

- $\Delta G = 0$: the reaction is at **equilibrium** and both $[A]$ and $[B]$ will not change:

$$A \rightleftharpoons B.$$

No need to find the value of ΔG for a Specific Reaction!

This might seem strange, given the key importance ΔG in determining whether or not a reaction will take place in a given direction. It turns out, however, that it is almost never necessary to explicitly evaluate ΔG. As we will show in the lesson that follows this one, it is far more convenient to work with the equilibrium constant of a reaction, within which ΔG is "hidden". This is just as well, because for most reactions (those that take place in solutions or gas mixtures) the value of ΔG depends on the **proportions** of the various reaction components in the mixture; it is not a simple sum of the "products minus reactants" type, as is the case with ΔH.

Recalling the condition for spontaneous change

$$\Delta G = \Delta H - T\Delta S < 0 \tag{13.3.7}$$

it is apparent that the temperature dependence of ΔG depends almost entirely on the entropy change associated with the process. (We say "almost" because the values of ΔH and ΔS are themselves slightly temperature dependent; both gradually increase with temperature). In particular, notice that in the above equation **the sign of the entropy change determines whether the reaction becomes more or less spontaneous as the temperature is raised.** For any given reaction, the sign of ΔH can also be positive or negative. This means that there are four possibilities for the influence that temperature can have on the spontaneity of a process:

Case 1: 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.

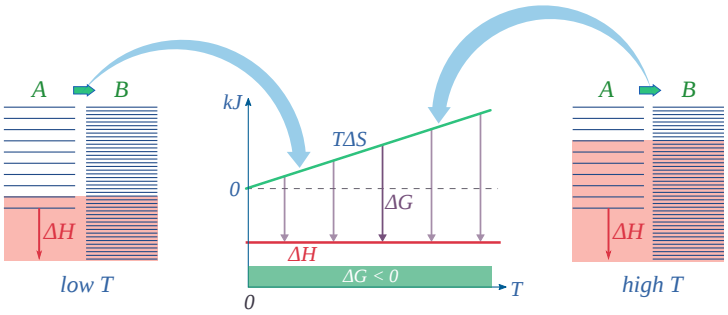


Figure 13.3.1: A hypothetical A ⟶ B reaction that is favored enthalpically and entropically (spontaneous at all temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

Case 2: 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.

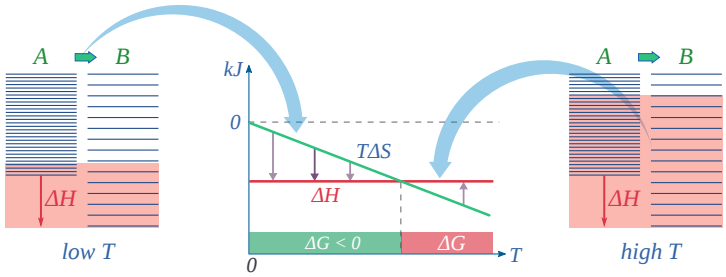


Figure 13.3.2: A hypothetical A ⟶ B reaction that is favored enthalpically and is not favored entropically (spontaneous at low temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

Case 3: $\Delta H > 0$ and $\Delta S > 0$

This is the reverse of the previous case; the entropy increase must overcome the handicap of an endothermic process so that $T\Delta S > \Delta H$. Since the effect of the temperature is to "magnify" the influence of a positive ΔS, the process will be spontaneous at temperatures above $T = \Delta H / \Delta S$. (Think of melting and boiling.)

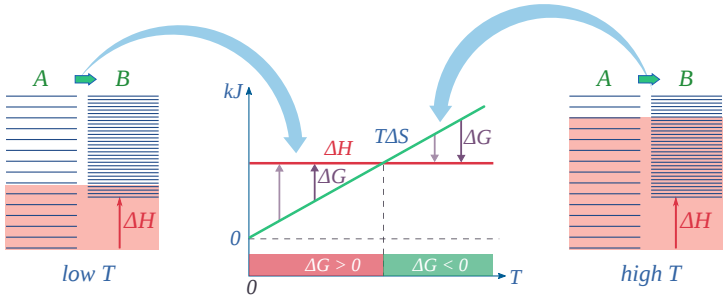


Figure 13.3.3: A hypothetical A ⟶ B reaction that is not favored enthalpically and is favored entropically (spontaneous at high temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

Case 4: $\Delta H > 0$ and $\Delta S < 0$

With both ΔH and ΔS working against it, this kind of process will not proceed spontaneously at any temperature. Substance A always has a greater number of accessible energy states, and is therefore always the preferred form.

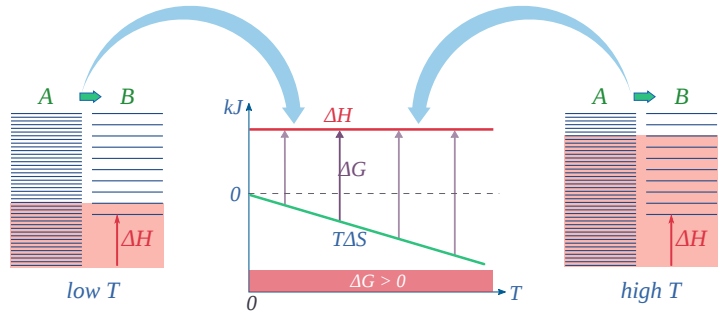


Figure 13.3.4: A hypothetical A ⟶ B reaction that is not favored enthalpically and is not is favored entropically (not spontaneous at temperatures). (CC BY 4.0; Ümit Kaya via LibreTexts)

The plots above are the important ones; do not try to memorize them, but make sure you understand and can explain or reproduce them for a given set of ΔH and ΔS.

- Their most important differentiating features are the position of the ΔH line (above or below the is $T\Delta S$ line), and the slope of the latter, which of course depends on the sign of ΔS.
- The reaction A → B will occur spontaneously only when ΔG is negative (blue arrows pointing down.)
- $T\Delta S$ plots are not quite straight lines as shown here. Similarly, the lines representing ΔH are even more curved.

The other two plots on each diagram are only for the chemistry-committed.

- Each pair of energy-level diagrams depicts the relative spacing of the microscopic energy levels in the reactants and products as reflected by the value of $\Delta S°$. (The greater the entropy, the more closely-spaced are the quantized microstates.)
- The red shading indicates the range of energy levels that are accessible to the system at each temperature. The spontaneous direction of the reaction will always be in the direction in which the red shading overlaps the greater number of energy levels, resulting in the maximum dispersal of thermal energy.
- Note that the vertical offsets correspond to $\Delta H°$ for the reaction.
- Never forget that it is the ability of thermal energy to spread into as many of these states as possible that determines the tendency of the process to take place. None of this is to scale, of course!

The Standard Gibbs Energy

You have already been introduced to the terms such as ΔU^o and ΔH^o in which the ^{o} sign indicates that all components (reactants and products) are in their *standard states*. This concept of standard states is especially important in the case of the free energy, so let's take a few moments to review it. More exact definitions of the conventional standard states can be found in most physical chemistry textbooks. In specialized fields such as biochemistry and oceanography, alternative definitions may apply. For example, the "standard pH" of zero (corresponding to $[H^+] = 1\ M$) is impractical in biochemistry, so pH = 7 is commonly employed. For most practical purposes, the following definitions are good enough:

- **gases:** 1 atmosphere partial pressure
- **pure liquids:** the liquid under a total (hydrostatic) pressure of 1 atm.
- **solutes:** an effective concentration of 1 mol L^{-1} (1 mol dm^{-3}). ("Effective" concentrations approach real concentrations as the latter approach zero; for practical purposes, these can be considered identical at real concentrations smaller than about 10^{-4} molar.)
- **solids:** the pure solid under 1 atm pressure

Reminder on Standard States

- There is actually no "standard temperature", but because most thermodynamics tables list values for 298.15 K (25° C), this temperature is usually implied.
- These same definitions apply to standard enthalpies and internal energies.
- Do not confuse these thermodynamic standard states with the "standard temperature and pressure" (STP) widely employed in gas law calculations.

To make use of Gibbs energies to predict chemical changes, we need to know the free energies of the individual components of the reaction. For this purpose we can combine the standard enthalpy of formation and the standard entropy of a substance to get its **standard free energy of formation**

$$\Delta G^o_f = \Delta H^o_f - T\Delta S^o_f \tag{13.3.8}$$

Recall that the symbol ° refers to the *standard state* of a substance measured under the conditions of 1 atm pressure or an effective concentration of 1 mol L^{-1} and a temperature of 298 K. Then determine the standard Gibbs energy of the reaction according to

$$\Delta G^o = \sum \Delta G^o_f \text{ (products)} - \sum \Delta G^o_f \text{ (reactants)} \tag{13.3.9}$$

As with standard heats of formation, the standard free energy of a substance represents the free energy change associated with the formation of the substance from the elements in their most stable forms as they exist under the standard conditions of 1 atm pressure and 298 K. Standard Gibbs free energies of formation are normally found directly from tables. Once the values for all the reactants and products are known, the standard Gibbs energy change for the reaction is found by Equation 13.3.8. Most tables of thermodynamic values list ΔG^o_f 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 13.3.1

Find the standard Gibbs energy change for the reaction

$$\mathrm{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}$$

The $\Delta G_f^{o\,\circ}$ values for the three components of this reaction system are $\mathrm{CaCO_3(s)}$: –1128 kJ mol^{-1}, CaO*(s)*: –603.5 kJ mol^{-1}, CO_2*(g)*: –137.2 kJ mol^{-1}.

Solution

Substituting into Equation 13.3.8, we have

$$\Delta G^o = (-603.5 - 137.2) - (-1128) kJ\,mol^{-1} = +130.9\ kJ\,mol^{-1}$$

This indicates that the process is not spontaneous under standard conditions (i.e., solid calcium carbone will not form solid calcium oxide and CO_2 at 1 atm partial pressure at 25° C).

Comment: This reaction is carried out on a huge scale to manufacture cement, so it is obvious that the process can be spontaneous under different conditions.

The practical importance of the Gibbs energy is that it allows us to make predictions based on the properties ($\Delta G°$ values) of the reactants and products themselves, eliminating the need to experiment. But bear in mind that while thermodynamics always correctly predicts whether a given process *can* take place (is spontaneous in the thermodynamic sense), it is unable to tell us if it *will* take place at an observable rate.

> *When thermodynamics says "no", it means exactly that. When it says "yes", it means "maybe".*

Example 13.3.2

The reaction

$$\mathrm{\tfrac{1}{2}O_2(g) + H_2(g) \rightarrow H_2O(l)}$$

is used in fuel cells to produce an electrical current. The reaction can also be carried out by direct combustion.

Thermodynamic data: molar entropies in J 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,

$$\begin{aligned}\Delta H^o &= \Delta H_f^p(\text{products}) - \Delta H_f^\circ(\text{reactants}) \\ &= -285.9\ kJ\,mol^{-1} - 0 \\ &= -285.9\ kJ\,mol^{-1}\end{aligned}$$

Similarly,

$$\begin{aligned}\Delta S^o &= S_f^o(\text{products}) - S_f^o(\text{reactants}) \\ &= (70.0) - (½ \times 205.0 + 130.6) \\ &= -163\ J\,K^{-1}mol^{-1}\end{aligned}$$

a. When the hydrogen and oxygen are combined directly, the heat released will be $\Delta H^o = -285.9\ kJ\,mol^{-1}$.

b. The maximum electrical work the fuel cell can perform is given by

$$\begin{aligned}\Delta G^o &= \Delta H^o - T\Delta S^o \\ &= -285.9\ kJ\,mol^{-1} - (298\ K)(-163\ JK^{-1}mol^{-1}). \\ &= -237.2\ kJ\,mol^{-1}.\end{aligned}$$

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:

$$\begin{aligned}\Delta H^o - \Delta G^o &= T\Delta S^o \\ &= (298\ K)(-163\ JK^{-1}mol^{-1}) \\ &= -48,800\ J\,mol^{-1} \\ &= -48.8\ kJ\,mol^{-1}.\end{aligned}$$

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 13.3.1: Standard Gibbs Energies of Select Substances

Stable Form	ΔG_f^o (kJ mol^{-1})	Unstable Form	ΔG_f^o (kJ mol^{-1})
$O_2(g)$	0	$O_3(g)$	163.2
C(graphite)	0	C(diamond)	2.9
S(rhombic)	0	S(monoclinic)	0.1
P(white)	0	$P_4(g)$	24.4

Ions in aqueous solution are a special case; their standard free energies are relative to the hydrated hydrogen ion $H^+(aq)$ which is assigned $\Delta G_f^o = 0$.

ΔG is very different from ΔG°. The distinction is nicely illustrated in Figure 13.3.5 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.

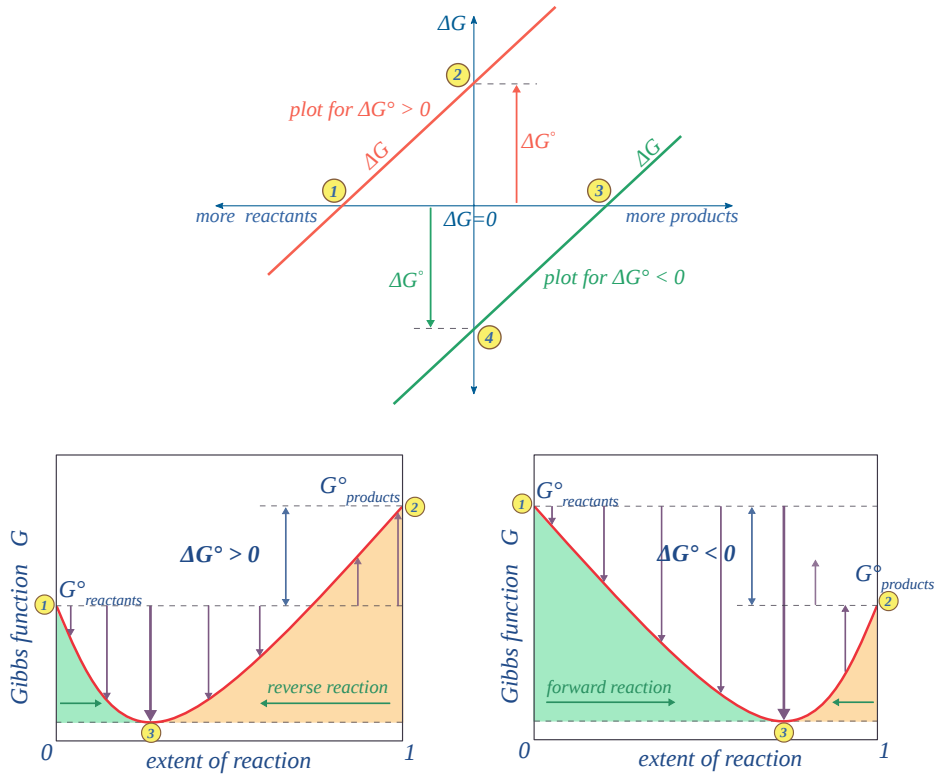


Figure 13.3.5: (CC BY 4.0; Ümit Kaya via LibreTexts)

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

$$4\,NH_3(g) + 5\,O_2(g) \rightarrow 4\,NO(g) + 6\,H_2O(g)$$

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:

$$2\,H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$$

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:

$$H_2O(g) \rightarrow 2\,H(g) + O(g)$$

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

$$N_2O_4(g) \rightarrow 2\,NO_2(g)$$

with $\Delta G^o = +2.8 kJ$.

in which the positive value of $\Delta G°$ tells us that N_2O_4 at 1 atm pressure will not change into two moles of NO_2 at the same pressure, but owing to the small absolute value of $\Delta G°$, we can expect the spontaneity of the process to be quite sensitive to

both the temperature (as shown in the table below) and to the pressure in exactly the way the Le Chatelier principle predicts.

Example

For reactions involving dissolved ions, one has to be quite careful. Thus for the dissociation of the weak hydrofluoric acid

$$\mathrm{HF(aq) \rightarrow H^+(aq) + F^-(aq)}$$

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:

$$\mathrm{H_2O(l) \rightarrow H^+(aq) + OH^-(aq)}$$

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:

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

with $\Delta G^o = 8.58\ kJ$.

Conversion of liquid water to its vapor at 1 atm partial pressure does not take place at 25° C, at which temperature the equilibrium partial pressure of the vapor (the "vapor pressure") is only 0.031 atm (23.8 torr.) Gaseous H_2O at a pressure of 1 atm can only exist at 100° C. Of course, water left in an open container at room temperature will spontaneously evaporate if the partial pressure of water vapor in the air is less than 0.031 atm, corresponding to a relative humidity of under 100%

Finding the Equilibrium Temperature

A reaction is in its equilibrium state when

$$\Delta G = \Delta H - T\Delta S = 0 \tag{13.3.10}$$

The temperature at which this occurs is given by

$$T = \frac{\Delta H}{\Delta S} \tag{13.3.11}$$

If we approximate ΔH by ΔH^o and ΔS by ΔS^o, so Equation 13.3.10would be

$$\Delta G \approx \Delta H^o - T\Delta S^o = 0 \tag{13.3.12}$$

We can then estimate the normal boiling point of a liquid. From the following thermodynamic data for water:

$H_2O(l)$	→	$H_2O(g)$	
−285.9		−241.8	$\Delta H°$ = +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

$$T = \frac{44,100\ J}{118.7\ J\,K^{-1}} = 371.5\ K \tag{13.3.13}$$

But "*the normal boiling point of water is 373 K*", you say? Very true. The reason we are off here is that both ΔH° and ΔS° have their own temperature dependencies; we are using the "standard" 25° values without correcting them to 100° C. Nevertheless, if you think about it, the fact that we can estimate the boiling point of a liquid from a table of thermodynamic data should be rather impressive! Of course, the farther one gets from 298 K, the more unreliable will be the result. Thus for the dissociation of dihydrogen into its atoms,

$H_2(g)$ → 2 $H(g)$

0 2 x (218.0) ΔH° = +436.0 kJ

130.6 2 x (114.6) ΔS° = +98.6 J K^{-1}

$$T = \frac{436,000\ J}{98.6\ JK^{-1}} = 4,420\ K \tag{13.3.14}$$

All one can say here is that H_2 will break down at something over 3000 K or so. (You may already know that *all* molecules will dissociate into their atoms at high temperatures.) We tend to think of high temperatures as somehow "forcing" molecules to dissociate into their atoms, but this is wrong. In order to get the H–H bond to vibrate so violently through purely thermal excitation that the atoms would fly apart, a temperature more like 30,000 K would be required. The proper interpretation is at the temperature corresponding to $\Delta H/T\Delta S$, 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

$$\mathrm{C(graphite) + O_2(g) \rightarrow CO_2(g)}$$

- $\Delta H^o = -393\ kJ$
- $\Delta G^o = -394\ kJ$ at $298\ K$

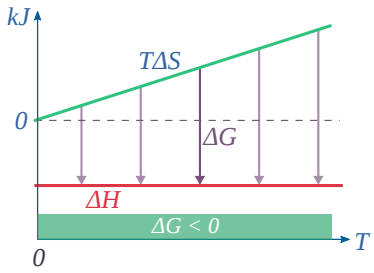


Figure 13.3.6: (CC BY 4.0; Ümit Kaya via LibreTexts)

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

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

- $\Delta H^o = -46.2\ kJ$
- $\Delta G^o = -16.4\ kJ$ at $298\ K$

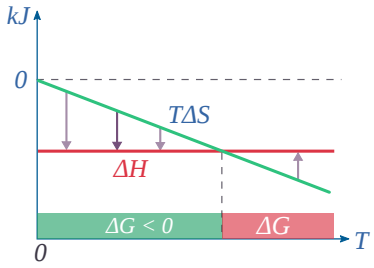


Figure 13.3.7: (CC BY 4.0; Ümit Kaya via LibreTexts)

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

$$N_2O_4(g) \rightarrow 2\,NO_2(g)$$

- $\Delta H^o = 55.3\ kJ$
- $\Delta G^o = +2.8\ kJ$ at $298\ K$

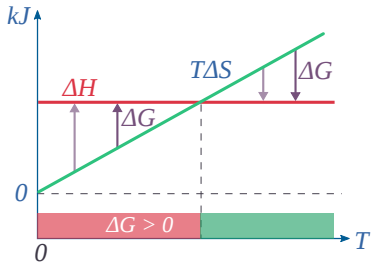


Figure 13.3.8: (CC BY 4.0; Ümit Kaya via LibreTexts)

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

$$\tfrac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$$

- $\Delta H^\circ = 33.2\ kJ$
- $\Delta S^o = -249\ J\,K^{-1}$
- $\Delta G^o = +51.3\ kJ$ at $298\ K$

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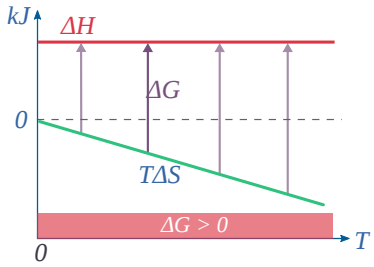


Figure 13.3.9: (CC BY 4.0; Ümit Kaya via LibreTexts)

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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13.4: 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. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \quad K_2 = 6.4 \times 10^{9}$

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:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2} \tag{13.4.1}$$

What is the relationship between K_1, K_2, and K_3, all at 100°C? The expression for K_1 has $[NO]^2$ in the numerator, the expression for K_2 has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for K_3. Multiplying K_1 by K_2 and canceling the $[NO]^2$ terms,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3 \tag{13.4.2}$$

Thus the product of the equilibrium constant expressions for K_1 and K_2 is the same as the equilibrium constant expression for K_3:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^{9}) = 1.3 \times 10^{-15} \tag{13.4.3}$$

The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions. In contrast, recall that according to Hess's Law, ΔH for the sum of two or more reactions is the sum of the ΔH values for the individual reactions.

Note

To determine K for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.

Example 13.4.6

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:

$$CO_{(g)} + \cancel{3H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)} \tag{13.4.4}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + \cancel{3H_{2(g)}} + H_{2(g)} \tag{13.4.5}$$

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \tag{13.4.6}$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^4) = 3.03 \times 10^3 \tag{13.4.7}$$

? Exercise 13.4.6

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. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$ $\quad K_1 = 4.4 \times 10^{53}$
2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ $\quad K_2 = 2.6 \times 10^{12}$
3. $\frac{1}{8}S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ $\quad K_3 = ?$

Answer

$K_3 = 1.1 \times 10^{66}$

Summary

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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13.5: Equilibrium Calculations for Gas-Phase and Heterogenous Reactions

Learning Objectives

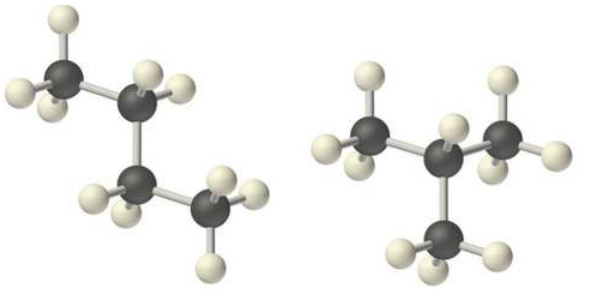
- To solve quantitative problems involving chemical equilibriums.

There are two fundamental kinds of equilibrium problems:

1. those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and
2. those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

Calculating an Equilibrium Constant from Equilibrium Concentrations

The equilibrium constant for the decomposition of $CaCO_{3(s)}$ to $CaO_{(s)}$ and $CO_{2(g)}$ is $K = [CO_2]$. At 800°C, the concentration of CO_2 in equilibrium with solid $CaCO_3$ and CaO is $2.5 \times 10^{-3}\ M$. Thus K at 800°C is 2.5×10^{-3} (remember that equilibrium constants are unitless). A more complex example of this type of problem is the conversion of n-butane, an additive used to increase the volatility of gasoline, into isobutane (2-methylpropane).



This reaction can be written as follows:

$$\mathrm{n\text{-}butane}_{(g)} \rightleftharpoons \mathrm{isobutane}_{(g)} \tag{13.5.1}$$

and the equilibrium constant $K = [\mathrm{isobutane}]/[\mathrm{n\text{-}butane}]$. At equilibrium, a mixture of n-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M n-butane. Substituting these concentrations into the equilibrium constant expression,

$$\begin{aligned} K &= \frac{[\mathrm{isobutane}]}{[\texttt{\textbackslash texT}n-butane]} \\ &= \frac{0.041\ M}{0.016\ M} \\ &= 2.6 \end{aligned}$$

Thus the equilibrium constant for the reaction as written is 2.6.

Example 13.5.1

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 13.5.1

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)}$$

A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained

- $1.37 \times 10^{-2}\ M\ HI$,
- $6.47 \times 10^{-3}\ M\ H_2$, and
- $5.94 \times 10^{-4}\ M\ I_2$.

Calculate K and K_p for this reaction.

Answer (K)

$K = 48.8$

Answer (K_p)

$K_p = 48.8$

Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example 13.5.2shows one way to do this.

Example 13.5.2

A 1.00 mol sample of $NOCl$ was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl_2. Calculate K at this temperature. The equation for the decomposition of $NOCl$ to NO and Cl_2 is as follows:

$$\mathrm{2\,NOCl(g) \rightleftharpoons 2\,NO(g) + Cl_2(g)}$$

Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium

Asked for: K

Strategy:

A. Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).
B. Calculate all possible initial concentrations from the data given and insert them in the table.
C. Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.
D. Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

Solution

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of $NOCl$, NO, and Cl_2 at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial			
Change			
Final			

B Initially, the system contains 1.00 mol of $NOCl$ in a 2.00 L container. Thus $[NOCl]_i = 1.00\ mol/2.00\ L = 0.500\ M$ The initial concentrations of NO and Cl_2 are 0 M because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f = 0.056\ mol/2.00\ L = 0.028\ M$ We insert these values into the following table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change			
Final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

$$\Delta[Cl_2] = 0.028\ M_{(final)} - 0.00\ M_{(initial)}] = +0.028\ M$$

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta[NO] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = 0.056\ M$$

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 13.5.2

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 13.5.1), for which K = 2.6 at 25°C. If we begin with a 1.00 M sample of n-butane, we can determine the concentration of n-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example 13.5.2

$$\text{n-butane}(g) \rightleftharpoons \text{isobutane}(g) \tag{13.5.2}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial		
Change		
Final		

The initial concentrations of the reactant and product are both known: [n-butane]i = 1.00 M and [isobutane]i = 0 M. We need to calculate the equilibrium concentrations of both n-butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the change in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as +x, then the change in the concentration of n-butane is Δ[n-butane] = −x. This is because the balanced chemical equation for the reaction tells us that 1 mol of n-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{13.5.3}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial	1.00	0
Change	−x	+x
Final	(1.00 − x)	(0 + x) = x

Substituting the expressions for the final concentrations of n-butane and isobutane from the table into the equilibrium equation,

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \frac{x}{1.00 - x} = 2.6 \tag{13.5.4}$$

Rearranging and solving for x,

$$\begin{aligned} x &= 2.6(1.00 - x) = 2.6 - 2.6x \\ x + 2.6x &= 2.6 \\ x &= 0.72 \end{aligned}$$

We obtain the final concentrations by substituting this x value into the expressions for the final concentrations of n-butane and isobutane listed in the table:

$$[\text{n-butane}]_f = (1.00 - x)M = (1.00 - 0.72)M = 0.28\ M \tag{13.5.5}$$

$$[\text{isobutane}]_f = (0.00 + x)M = (0.00 + 0.72)M = 0.72\ M \tag{13.5.6}$$

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same K that we used in the calculation:

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \left(\frac{0.72\ \cancel{M}}{0.28\ \cancel{M}}\right) = 2.6 \tag{13.5.7}$$

This is the same K we were given, so we can be confident of our results.

Example 13.5.3 illustrates a common type of equilibrium problem that you are likely to encounter.

Example 13.5.3

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 13.5.3

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 13.5.3, 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 13.5.4

✔ Example 13.5.4

In the water–gas shift reaction shown in Example 13.5.3, 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 13.5.3, 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 13.5.4

The exercise in Example 13.5.1 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 13.5.5.

Example 13.5.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$\mathrm{N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)} \tag{13.5.8}$$

with $K_p = 2.0 \times 10^{-31}$ at 25°C.

What is the partial pressure of NO in equilibrium with N_2 and O_2 in the atmosphere (at 1 atm) $P_{N_2} = 0.78\ atm$ and $P_{O_2} = 0.21\ atm$?

Given: balanced equilibrium equation and values of K_p, P_{O_2}, and P_{N_2}

Asked for: partial pressure of NO

Strategy:

A. Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.
B. Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration (x).
C. Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for K.

Solution

A Because we are given Kp and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of O_2 is 0.21 atm and that of N_2 is 0.78 atm. If we define the change in the partial pressure of NO as 2x, then the change in the partial pressure of O_2 and of N_2 is −x because 1 mol each of N_2 and of O_2 is consumed for every 2 mol of NO produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

$$\mathrm{N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)} \tag{13.5.9}$$

ICE	P_{N_2}	P_{O_2}	P_{NO}
Initial	0.78	0.21	0
Change	−x	−x	+2x
Final	(0.78 − x)	(0.21 − x)	2x

B Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78 - x)(0.21 - x)} = 2.0 \times 10^{-31}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very small; therefore, the x value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, (0.78 − x) = 0.78 and (0.21 − x) = 0.21. Substituting these expressions into our original equation,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4}$$

$$x^{=} 9.1 \times 10^{-17}$$

C Substituting this value of x into our expressions for the final partial pressures of the substances,

- $P_{NO} = 2x\ atm = 1.8 \times 10^{-16}\ atm$
- $P_{N_2} = (0.78 - x)\ atm = 0.78\ atm$
- $P_{O_2} = (0.21 - x)\ atm = 0.21\ atm$

From these calculations, we see that our initial assumption regarding x was correct: given two significant figures, 2.0×10^{-16} is certainly negligible compared with 0.78 and 0.21. When can we make such an assumption? As a general rule, if x is less than about 5% of the total, or $10^{-3} > K > 10^{3}$, then the assumption is justified. Otherwise, we must use the quadratic formula or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of N_2 and O_2 to a substantial degree at 25°C. We can verify our results by substituting them into the original equilibrium equation:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

The final K_p agrees with the value given at the beginning of this example.

? Exercise 13.5.5

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 13.5.6

✔ Example 13.5.6

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 13.5.5. 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 13.5.6

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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13.6: Reaction Directions (Empirical Explanation)

Learning Objectives

- To predict in which direction a reaction will proceed.
- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

We previously saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

The Reaction Quotient

To determine whether a system has reached equilibrium, chemists use a quantity called the Reaction Quotient (Q). The expression for the Reaction Quotient has precisely the same form as the equilibrium constant expression from the Law of Mass Action, except that Q may be derived from a set of values measured at any time during the reaction of any mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:

$$aA + bB \rightarrow cC + dD \tag{13.6.1}$$

the Reaction Quotient is defined as follows:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{13.6.2}$$

To understand how information is obtained using a Reaction Quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,

$$\mathrm{N_2O_4(g) \rightleftharpoons 2\,NO_2(g).} \tag{13.6.3}$$

For this reaction, $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

$$Q = \frac{[NO_2]^2}{[N_2O_4]} \tag{13.6.4}$$

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of Q were calculated for each. Each experiment begins with different proportions of product and reactant:

Table 13.6.1: Three Conditions of the dissociation of dinitrogen tetroxide to nitrogen dioxide (Equation 13.6.1)

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 13.6.1.

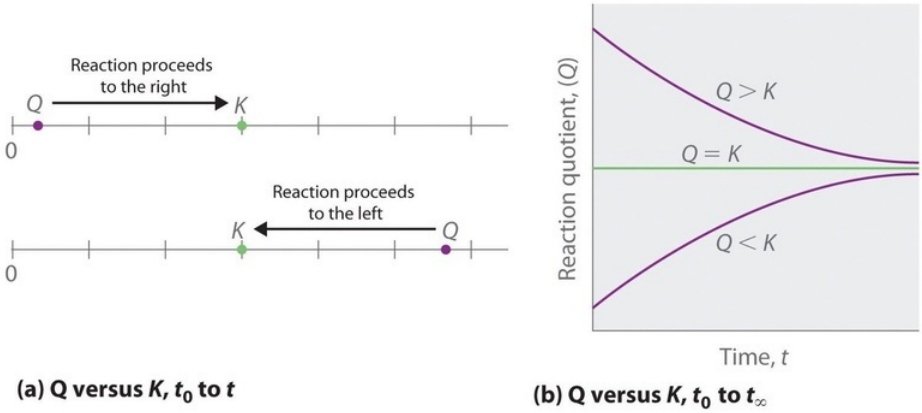


Figure 13.6.1: Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K.(a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K. (b) The change in the composition 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 13.6.1: 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 13.6.2to 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:

$$\begin{aligned} Q &= \frac{[CO][H_2]^3}{[CH_4][H_2O]} \\ &= \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})} \\ &= 9.0 \times 10^{-6} \end{aligned}$$

Because $K = 2.4 \times 10^{-4}$, we see that $Q < K$. Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming H_2 and CO at the expense of H_2O and CH_4.

? Exercise 13.6.1

In the water–gas shift reaction introduced in Example 13.6.1, 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 H_2O, 0.0080 mol of CO_2, and 0.012 mol of H_2 are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

Answer

$Q = 0.96$ (Q > K), so the reaction will proceed to the left, and CO and H_2O will form.

Predicting the Direction of a Reaction with a Graph

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which $Q = K$. Such a graph allows us to predict what will happen to a reaction when conditions change so that Q no longer equals K, such as when a reactant concentration or a product concentration is increased or decreased.

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:

$$\mathrm{PbCO_3(s) \rightleftharpoons PbO(s) + CO_2(g)} \tag{13.6.5}$$

Because $PbCO_3$ and PbO are solids, the equilibrium constant is simply $K = [CO_2]$. At a given temperature, therefore, any system that contains solid $PbCO_3$ and solid PbO will have exactly the same concentration of CO_2 at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure 13.6.2, 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 13.6.2 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 13.6.5 will proceed to the left as written, until $[CO_2] = K$. Conversely, the point labeled B in Figure 13.6.2 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 13.6.5 will therefore proceed to the right as written, until $[CO_2] = K$.

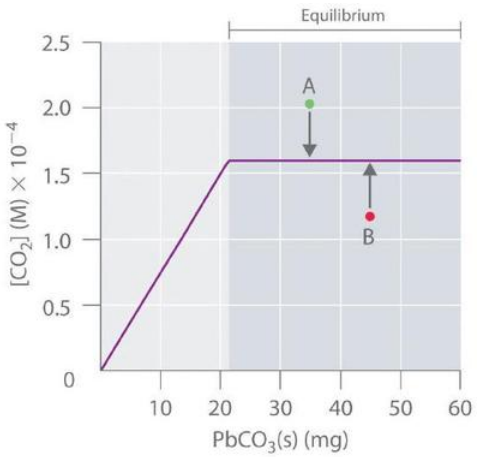


Figure 13.6.2: The Concentration of Gaseous CO_2 in a Closed System at Equilibrium as a Function of the Amount of Solid $PbCO_3$ Added. Initially the concentration of CO2(g) increases linearly with the amount of solid $PbCO_3$ added, as $PbCO_3$ decomposes to CO2(g) and solid PbO. Once the CO_2 concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $PbCO_3$ has no effect on $[CO_2]$, as long as the temperature remains constant.

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:

$$\mathrm{CdO(s) + H_2(g) \rightleftharpoons Cd(s) + H_2O(g)} \tag{13.6.6}$$

and the equilibrium constant K is $[H_2O]/[H_2]$. If $[H_2O]$ is doubled at equilibrium, then [H2] must also be doubled for the system to remain at equilibrium. A plot of $[H_2O]$ versus $[H_2]$ at equilibrium is a straight line with a slope of K (Figure 13.6.3). 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 13.6.6 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point A in Figure 13.6.3 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 13.6.6 will proceed to the right as written, consuming H_2 and producing H_2O, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point B in Figure 13.6.3 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 13.6.6 will proceed to the left as written, consuming H_2O and producing H_2, which causes the concentration ratio to move down and to the right toward the equilibrium line.

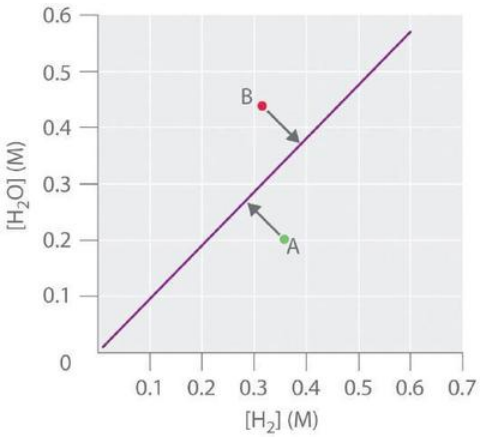


Figure 13.6.3: The Concentration of Water Vapor versus the Concentration of Hydrogen for the $CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)}$ System at Equilibrium. For any equilibrium concentration of $H_2O_{(g)}$, there is only one equilibrium concentration of H2(g). Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]$ at equilibrium requires a large $[H_2]$ and vice versa. In this case, the slope of the line is equal to K.

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:

$$NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)} \tag{13.6.7}$$

For this system, K is equal to the product of the concentrations of the two products: $[NH_3][HI]$. If we double the concentration of NH3, the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure 13.6.4 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 13.6.4) corresponds to $Q < K$, and the reaction in Equation 13.6.7 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point B in Figure 13.6.4) corresponds to $Q > K$, and the reaction in Equation 13.6.7 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

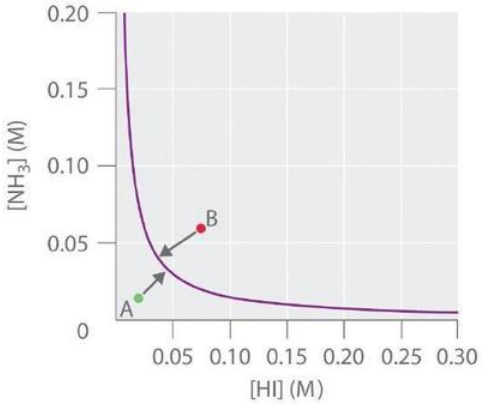


Figure 13.6.4: The Concentration of $NH_{3(g)}$ versus the Concentration of $HI_{(g)}$ for the $NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)}$ System at Equilibrium. Only one equilibrium concentration of $NH_{3(g)}$ is possible for any given equilibrium concentration of HI(g). In this case, the two are inversely proportional. Thus a large $[HI]$ at equilibrium requires a small $[NH_3]$ at equilibrium and vice versa.

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_p). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.



Video 13.6.1: See www.youtube.com/watch?v=pnU7ogsgUW8 to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

$$2\,NO_{(g)} + O_{2(g)} \rightleftharpoons 2\,NO_{2(g)} \tag{13.6.8}$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \tag{13.6.9}$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the Reaction Quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \quad \Delta H = -9.4\ \text{kJ (exothermic)} \tag{13.6.10}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) + \text{heat} \tag{13.6.11}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between NO_2 and N_2O_4 in this reaction

$$N_2O_{4(g)} \rightleftharpoons 2\,NO_{2(g)} \quad \Delta H = 57.20\ \text{kJ} \tag{13.6.12}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\text{heat} + N_2O_{4(g)} \rightleftharpoons 2\,NO_{2(g)} \tag{13.6.13}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown color to fade.

Temperature is Neither a Reactant nor Product

It is not uncommon that textbooks and instructors to consider heat as a independent "species" in a reaction. While this is rigorously incorrect because one cannot "add or remove heat" to a reaction as with species, it serves as a convenient mechanism to predict the shift of reactions with changing temperature. For example, if heat is a "reactant" ($\Delta H > 0$), then the reaction favors the formation of products at elevated temperature. Similarly, if heat is a "product" ($\Delta H < 0$), then the reaction favors the formation of reactants. A more accurate, and hence preferred, description is discussed below.

Example 13.6.2: Steam Reforming of Methane

The commercial production of hydrogen is carried out by treating natural gas with steam at high temperatures and in the presence of a catalyst (“steam reforming of methane”):

$$\mathrm{CH_4 + H_2O \rightleftharpoons CH_3OH + H_2}$$

Given the following boiling points: CH_4 (methane) = –161°C, H_2O = 100°C, CH_3OH = 65°, H_2 = –253°C, predict the effects of an increase in the total pressure on this equilibrium at 50°, 75° and 120°C.

Solution

To identify the influence of changing pressure on the three reaction conditions, we need to identify the correct reaction including the phase of each reactant and product. Calculate the change in the moles of gas for each process:

Temperature	Equation	Δn_g	shift
50°	$\mathrm{CH_4(g) + H_2O(l) \rightarrow CH_3OH(l) + H_2(g)}$	0	none
75°	$\mathrm{CH_4(g) + H_2O(l) \rightarrow CH_3OH(g) + H_2(g)}$	+1	to left
120°	$\mathrm{CH_4(g) + H_2O(g) \rightarrow CH_3OH(g) + H_2(g)}$	0	none

Exercise 13.6.2

What will happen to the equilibrium when the volume of the system is decreased?

$$\mathrm{2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)}$$

Answer

Decreasing the volume leads to an increase in pressure which will cause the equilibrium to shift towards the side with fewer moles. In this reaciton, there are three moles on the reactant side and two moles on the product side, so the new equilibrium will shift towards the products (to the right).

Summary

The Reaction Quotient (Q) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction. Reaction Quotient:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The Reaction Quotient (Q or Q_p) has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium, $Q = K$. Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium.

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Footnotes

1. 1 Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle

when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium

concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress

change to a reaction's conditions that may cause a shift in the equilibrium

Contributors and Attributions

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13.7: Reaction Directions (Thermodynamic Explanation)

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously:

- $\Delta S_{univ} > 0$ (2nd law of thermodynamics),
- $\Delta G_{sys} < 0$ (Gibbs Energy version), and
- the relative magnitude of the reaction quotient Q versus the equilibrium constant K.

Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table 13.7.1 summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table 13.7.1: Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
Q < K	Q = K	Q > K

*Spontaneous in the reverse direction.

Because all three criteria assess the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the standard free energy of reaction (ΔG°) and the equilibrium constant (K).

Free Energy and the Equilibrium Constant

Because ΔH° and ΔS° determine the magnitude of ΔG° and because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG° and vice versa. "Free Energy", ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. The general relationship can be shown as follow (derivation not shown):

$$\Delta G = V\Delta P - S\Delta T \tag{13.7.1}$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation 13.7.1 simplifies to

$$\Delta G = V\Delta P \tag{13.7.2}$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the V in Equation 13.7.2 by nRT/P (where n is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f, respectively):

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P \tag{13.7.3}$$

$$= nRT\frac{\Delta P}{P} = nRT\ln\left(\frac{P_f}{P_i}\right) \tag{13.7.4}$$

If the initial state is the standard state with P_i = 1 atm, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G^\circ = nRT \ln P \tag{13.7.5}$$

This can be rearranged as follows:

$$G = G^\circ + nRT \ln P \tag{13.7.6}$$

As you will soon discover, Equation 13.7.6 allows us to relate ΔG^o and K_p. Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA + bB \rightleftharpoons cC + dD \tag{13.7.7}$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

$$\Delta G = \sum_m G_{products} - \sum_n G_{reactants} \tag{13.7.8}$$

$$= (cG_C + dG_D) - (aG_A + bG_B) \tag{13.7.9}$$

Substituting Equation 13.7.6 for each term into Equation 13.7.9,

$$\Delta G = [(cG^o_C + cRT \ln P_C) + (dG^o_D + dRT \ln P_D)] - [(aG^o_A + aRT \ln P_A) + (bG^o_B + bRT \ln P_B)] \tag{13.7.10}$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_{\mathrm{C}}^c P_{\mathrm{D}}^d}{P_{\mathrm{A}}^a P_{\mathrm{B}}^b} \right) \tag{13.7.11}$$

$$= \Delta G^\circ + RT \ln Q \tag{13.7.12}$$

where ΔG° indicates that all reactants and products are in their standard states. For gases at equilibrium ($Q = K_p$,), and as you've learned in this chapter, $\Delta G = 0$ for a system at equilibrium. Therefore, we can describe the relationship between ΔG^o and K_p for gases as follows:

$$0 = \Delta G^\circ + RT \ln K_p \tag{13.7.13}$$

$$\Delta G^\circ = -RT \ln K_p \tag{13.7.14}$$

If the products and reactants are in their standard states and $\Delta G° < 0$, then $K_p > 1$, and products are favored over reactants. Conversely, if $\Delta G° > 0$, then $K_p < 1$, and reactants are favored over products. If $\Delta G° = 0$, 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 13.7.3). 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.

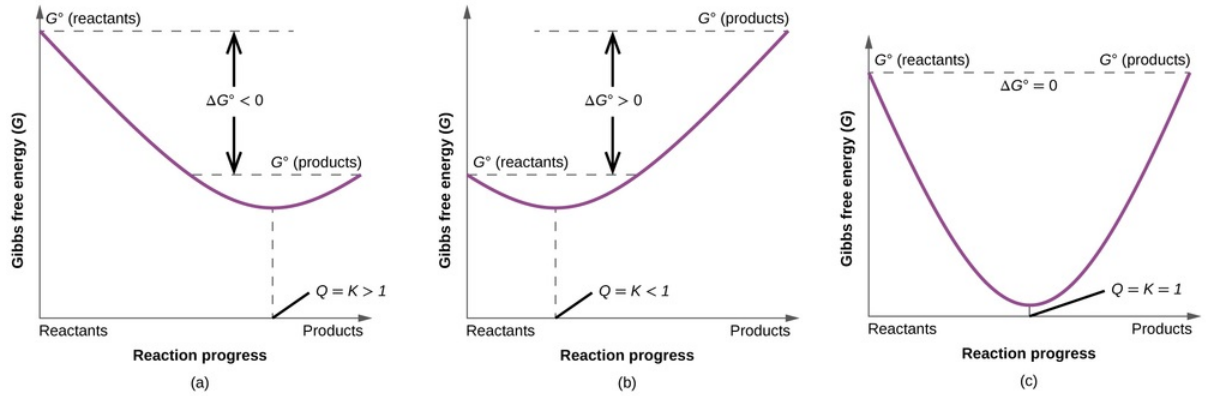


Figure 13.7.1: These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium. (CC BY 4.0; OpenStax).

Example 13.7.2

ΔG^o is −32.7 kJ/mol of N_2 for the reaction

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

This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions:

- P_{N_2} = 2.00 atm,
- P_{H_2} = 7.00 atm,
- P_{NH_3} = 0.021 atm,
- and T = 100°C.

Does the reaction favor products or reactants?

Given: balanced chemical equation, partial pressure of each species, temperature, and ΔG°

Asked for: whether products or reactants are favored

Strategy:

A. Using the values given and Equation 13.7.12, calculate Q.
B. Substitute the values of ΔG° and Q into Equation 13.7.12to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG° and ΔG under nonstandard conditions is given in Equation 13.7.12 Substituting the partial pressures given, we can calculate Q:

$$Q = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7}$$

B Substituting the values of ΔG° and Q into Equation 13.7.12,

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q \\ &= -32.7\ \text{kJ} + \left[(8.314\ \text{J/K})(373\ \text{K})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)\ln(6.4 \times 10^{-7})\right] \\ &= -32.7\ \text{kJ} + (-44\ \text{kJ}) \\ &= -77\ \text{kJ/mol of } N_2\end{aligned}$$

Because ΔG < 0 and Q < 1.0, the reaction is spontaneous to the right as written, so products are favored over reactants.

Exercise 13.7.2

Calculate ΔG for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: T = 50°C, P_{NO} = 0.0100 atm, P_{O_2} = 0.200 atm, and P_{NO_2} = 1.00 × 10^{-4} atm. The value of ΔG° for this reaction is −72.5 kJ/mol of O_2. Are products or reactants favored?

Answer

−92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written, so products are favored.

Example 13.7.3

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 13.7.2, ΔG°, and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG° and T (in kelvin) into Equation 13.7.14to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution

In Example 10, we used tabulated values of ΔG°_f to calculate ΔG° for this reaction (−32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 13.7.14,

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

$$\frac{-\Delta G^\circ}{RT} = \ln K_p$$

Inserting the value of ΔG° and the temperature (25°C = 298 K) into this equation,

$$\ln K_p = -\frac{(-32.7\ \text{kJ})(1000\ \text{J/kJ})}{(8.314\ \text{J/K})(298\ \text{K})} = 13.2$$

$$K_p = 5.4 \times 10^5$$

Thus the equilibrium constant for the formation of ammonia at room temperature is favorable. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

Exercise 13.7.3

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. ΔG° for this reaction is −70.5 kJ/mol of O_2.

Answer

2.2 × 10^{12}

Although K_p is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant K is defined in terms of the concentrations of the reactants and the products. We described the relationship between the numerical magnitude of \(K_p\) and K previously and showed that they are related:

$$K_p = K(RT)^{\Delta n} \tag{13.7.15}$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 13.7.14can be written in a more general form:

$$\Delta G^\circ = -RT \ln K \tag{13.7.16}$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 13.7.16 for the difference between K_p and K. Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of **activities** or **fugacities** in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

Combining Equations 13.7.16 with $\Delta G^o = \Delta H^o - T\Delta S^o$ provides insight into how the components of ΔG° influence the magnitude of the equilibrium constant:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K \tag{13.7.17}$$

Notice that K becomes larger as ΔS° becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as ΔH° decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

> *The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder and seek the lowest energy state possible.*

Temperature Dependence of the Equilibrium Constant

The fact that ΔG° and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 13.7.17, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{13.7.18}$$

Assuming ΔH° and ΔS° are temperature independent, for an exothermic reaction (ΔH° < 0), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction (ΔH° > 0), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 13.7.18agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 13.7.18 also shows that the magnitude of ΔH° dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS° affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH° for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS°. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying Equation 13.7.18gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \tag{13.7.19}$$

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \tag{13.7.20}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{13.7.21}$$

Thus calculating ΔH° from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH° and ΔS° are independent of temperature. Equation 13.7.21is often referred to as the **van 't Hoff equation** after Dutch chemist Jacobus Henricus van 't Hoff in 1884 in his book Études de Dynamique chimique (Studies in dynamic chemistry).

Example 13.7.4

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 13.7.2 What is K_p at 500°C? (Use the data from Example 13.7.1)

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 13.7.21to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of ΔH° for the reaction obtained using Hess's law is −91.8 kJ/mol of N_2. If we set T_1 = 25°C = 298 K and T_2 = 500°C = 773 K, then from Equation 13.7.21we obtain the following:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$= \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{8.314\ \text{J/K}}\left(\frac{1}{298\ \text{K}} - \frac{1}{773\ \text{K}}\right) = -22.8$$

$$\frac{K_2}{K_1} = 1.3 \times 10^{-10}$$

$$K_2 = (5.4 \times 10^5)(1.3 \times 10^{-10}) = 7.0 \times 10^{-5}$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

Exercise 13.7.4

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 13.7.4to calculate K_p for this reaction at 1000°C.

Answer

5.6×10^{-4}

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial pressures of the reactants and products, which gives us a relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If ΔG° < 0, then K or K_p > 1, and products are favored over reactants. If ΔG° > 0, then K or K_p < 1, and reactants are favored over products. If ΔG° = 0, then K or K_p = 1, and the system is at equilibrium. We can use the measured equilibrium constant K at one temperature and ΔH° to estimate the equilibrium constant for a reaction at any other temperature.

Contributors and Attributions

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13.8: Distribution of a Single Species between Immiscible Phases - Extraction and Separation

A partitioning of a compound exist between a mixture of two immiscible phases at equilibrium, which is a measure of the difference in solubility of the compound in these two phases. If one of the solvents is a gas and the other a liquid, the "gas/liquid partition coefficient" is the same as the dimensionless form of the Henry's law constant. A solute can partition when one or both solvents is a solid (e.g., solid solution).

Liquid-Liquid Extractions

We call the process of moving a species from one phase to another phase an **extraction**. Simple extractions are particularly useful for separations where only one component has a favorable partition coefficient. Several important separation techniques are based on a simple extraction, including liquid–liquid, liquid–solid, solid–liquid, and gas–solid extractions. The most important group of separation techniques uses a selective partitioning of the solute between two immiscible phases. If we bring a phase containing a solute, S, into contact with a second phase, the solute partitions itself between the two phases, as shown by the following equilibrium reaction.

$$\mathrm{S_{phase\,1}} \rightleftharpoons \mathrm{S_{phase\,2}} \tag{13.8.1}$$

The equilibrium constant for this equilbrium is

$$K_\mathrm{D} = \frac{[\mathrm{S_{phase\ 2}}]}{[\mathrm{S_{phase\ 1}}]} \tag{13.8.2}$$

is called the distribution constant or **partition coefficient**. If K_D is sufficiently large, then the solute moves from phase 1 to phase 2. The solute remains in phase 1 if the partition coefficient is sufficiently small. When we bring a phase containing two solutes into contact with a second phase, if K_D is favorable for only one of the solutes a separation of the solutes is possible. The physical states of the phases are identified when describing the separation process, with the phase containing the sample listed first. For example, if the sample is in a liquid phase and the second phase is a solid, then the separation involves liquid–solid partitioning.

It often happens that two immiscible liquid phases are in contact, one of which contains a solute. How will the solute tend to distribute itself between the two phases? One's first thought might be that some of the solute will migrate from one phase into the other until it is distributed equally between the two phases, since this would correspond to the maximum dispersion (randomness) of the solute. This, however, does not take into the account the differing solubilities the solute might have in the two liquids; if such a difference does exist, the solute will preferentially migrate into the phase in which it is more soluble (Figure 13.8.1).

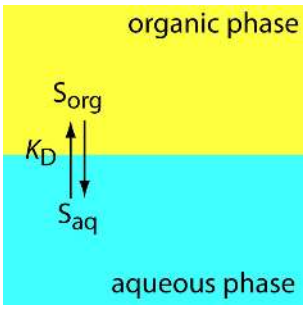


Figure 13.8.1: Scheme for a simple liquid–liquid extraction in which the solute's partitioning depends only on the K_D equilibrium.

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 13.8.2: A separatory funnel with two solvents.

If the distribution ratio is too low to achieve efficient separation in a single step, it can be repeated; there are automated devices that can carry out hundreds of successive extractions, each yielding a product of higher purity. In these applications our goal is to exploit the Le Chatelier principle by repeatedly upsetting the phase distribution equilibrium that would result if two phases were to remain in permanent contact.



Video 13.8.1: How to perform a liquid-liquid extraction using a separating funnel.

Example 13.8.1

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.

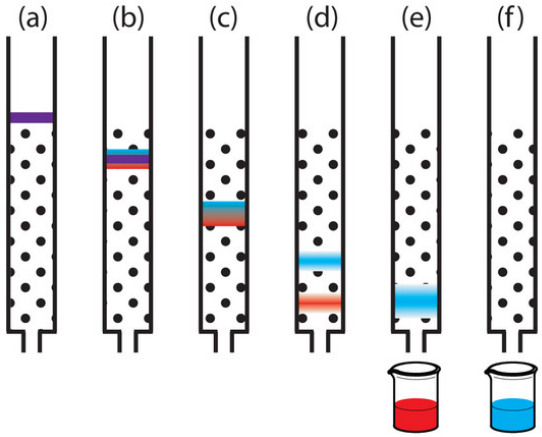


Figure 13.8.3: Progress of a column chromatographic separation of a two-component mixture. In (a) the sample is layered on top of the stationary phase. As mobile phase passes through the column, the sample separates into two solute bands (b–d). In (e) and (f), we collect each solute as it elutes from 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 13.8.3 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 13.8.1*a*). As the sample moves down the column the solutes begin to separate (Figures 13.8.1*b*, *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 13.8.1*d*).

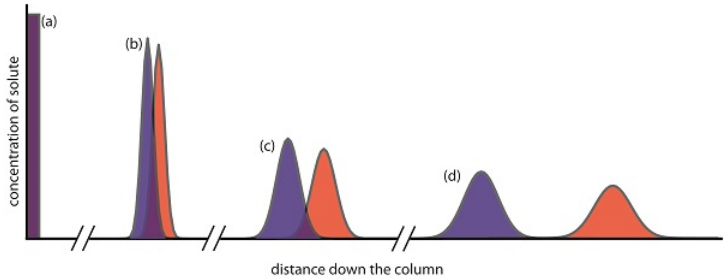


Figure 13.8.4: An alternative view of the separation in Figure 13.8.3 showing the concentration of each solute as a function of distance down the column.

We can follow the progress of the separation either by collecting fractions as they elute from the column (Figure 13.8.4), 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 13.8.5), and consists of a peak for each solute.

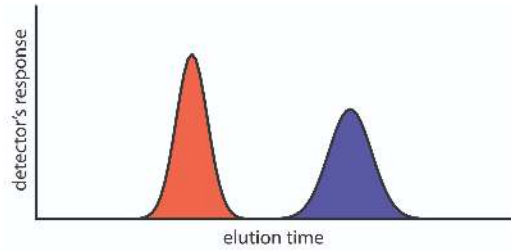


Figure 13.8.5: Chromatogram for the separation shown in Figure 13.8.3 showing the detector's response as a function of the elution time.

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13.E: Chemical Equilibria (Exercises)

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

Q1

Write an expression for the equilibrium constant K_c for each reaction below.

a. $2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$
b. $N_2H_4(g) + 3\,O_2(g) \rightleftharpoons 2\,NO_2(g) + H_2O(g)$
c. $O_3(g) + H_2O(l) \rightleftharpoons H_2(g) + 2\,O_2(g)$

Solution

For a general reaction $aA + bB \rightleftharpoons cC + dD$ then Law of Mass Action argues we can construct an equilibrium constant thusly

$$K_c = \frac{[C]c[D]d}{[A]a[B]b}$$

This is the general equations to substitute the reactants and product concentrations (with coefficients as exponents).

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

a. $K_c = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$
b. $K_c = \dfrac{[H_2O][NO_2]^2}{[N_2H_4][O_2]^3}$
c. $K_c = \dfrac{[O_2]^2[H_2]}{[O_3]}$

Note that for part c, $H_2O(l)$ is not included because pure solids and liquids are not included in the equilibrium constant.

Q3

Gaseous chlorine reacts with water vapor to form hydrogen chloride and oxygen gas. Write down the equilibrium expression (K_p) for the reaction.

Solution

First, a balanced reaction is constructed to ensure the equilibrium expression will be correctly states.

$$2\,Cl_2 + 2\,H_2O \rightleftharpoons 4\,HCl + O_2$$

Equilibrium expression K_p is as follows:

$$K_p = \frac{p_{HCl}^4 p_{O_2}}{p_{Cl_2}^2 p_{H_2O}^2}$$

Q11

For each thermodynamics equilibrium expressions outlined below, determine one possible chemical reaction related to each.

a. $$K = \frac{a\{CO\}^2}{a\{CO_2\}}$$

b. $$K = \frac{a\{H_2O\}^2}{a\{H_2\}^2 a\{O_2\}}$$

c. $$K = \frac{a\{Cl_2O\}^2}{a\{Cl_2\}^2 a\{O_2\}}$$

d. $$K = \frac{a\{COCl_2\}}{a\{CO\} \cdot a\{Cl_2\}}$$

Solution

a. $$CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)$$

b. $$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g)$$

c. $$2\,Cl_2(g) + O_2(g) \rightleftharpoons 2\,Cl_2O(g)$$

d. $$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

Q15A

Based on the following data, calculate the equilibrium constant and the value of ΔG at 273 K.

a. $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$ with

- $[CO_2]_{eq} = 0.0954\,M$
- $[H_2]_{eq} = 0.0454\,M$
- $[CO]_{eq} = 0.0046\,M$
- $[H_2O]_{eq} = 0.0046\,M$

b. $2\,NO(g) + 2\,H_2(g) \rightleftharpoons N_2(g) + 2\,H_2O(g)$ with

- $[NO]_{eq} = 0.45\,M$
- $[H_2]_{eq} = 0.63\,M$
- $[N_2]_{eq} = 0.95\,M$
- $[H_2O]_{eq} = 1.3\,M$

Solution

a)

$$K = \frac{[CO][H_2O]}{[CO_2][H_2]}$$
$$= \frac{(0.0046)(0.0046)}{(0.0954)(0.0454)}$$
$$= 4.9 \times 10^{-3}$$

$$\Delta G = RT\ln(K) = (8.3145\,J/(K\,mol))(273\,K)\ln(4.9 \times 10^{-3}) = -12072.288\,J/mol$$

b)

$$K = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2} = \frac{[0.95][1.3]^2}{[0.45]^2[0.63]^2} = 19.98$$

$$\Delta G = RT\ln(K) = (8.3145\,J/K\,mol)(273\,K)\ln(19.98) = 6797.62\,J/mol$$

Q15B

Calculate the appropriate K value for the following reactions using the information provided. Assume that they are preformed under standard conditions (and 298.15 K).

a. $$2\,NO_2(g) \rightleftharpoons 2\,NO(g) + O_2(g)$$

b. $$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

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:

$$2\,CH_4(g) + 3\,O_2(g) \rightleftharpoons 2\,CO(g) + 4\,H_2O(g)$$

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:

$$\Delta G^\circ_{rxn} = -RT\ln(K_p)$$

Relevant Information obtained from the thermodynamic tables

$\Delta G_f^\circ\ NO_2(g) = 51.30\frac{kJ}{mol}$ $\Delta G_f^\circ\ H_3O^+(aq) = -103.45\frac{kJ}{mol}$

$\Delta G_f^\circ\ NO(g) = 86.57\frac{kJ}{mol}$ $\Delta G_f^\circ\ NH_3(aq) = -26.5\frac{kJ}{mol}$

$\Delta G_f^\circ\ O_2(g) = 0\frac{kJ}{mol}$ $\Delta G_f^\circ\ CH_4(g) = -50.84\frac{kJ}{mol}$

$\Delta G_f^\circ\ NH_4^+(aq) = -79.37\frac{kJ}{mol}$ $\Delta G_f^\circ\ CO(g) = -137.28\frac{kJ}{mol}$

$\Delta G_f^\circ\ H_2O(l) = -237.14\frac{kJ}{mol}$ $\Delta G_f^\circ\ H_2O(g) = -228.61\frac{kJ}{mol}$

Note that the relationship here is between ΔG and K_p, which is:

$$K_p \approx \frac{P_{products}}{P_{reactants}}$$

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).

$$\Delta G^\circ = \sum n_{products} \times \Delta G^\circ_{f_{products}} - \sum n_{reactants} \times \Delta G^\circ_{f_{reactants}}$$

$$\Delta G^\circ(2\,NO_2(g) \rightleftharpoons 2\,NO(g) + O_2(g)) = 70.42\ \frac{kJ}{mol}$$

$$\Delta G^\circ(NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)) = -437.93\frac{kJ}{mol}$$

$$\Delta G^\circ(2\,CH_4(g) + 3\,O_2(g) \rightleftharpoons 2\,CO(g) + 4\,H_2O(l)) = -1121.44\frac{kJ}{mol}$$

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!!)

$$\Delta G^\circ_{rxn} = -\left(8.314\ \frac{J}{mol\,K}\right)(298.15\,K) \times \ln(K_p)$$

$$70.54\frac{kJ}{mol} = -\left(8.314\frac{J}{mol\,K}\right)(298.15\,K) \times \ln(K_p)$$

$$-\frac{70.54\,\frac{\text{kJ}}{\text{mol}}}{\left(8.314\,\frac{\text{J}}{\text{molK}}\right)(298.15\,\text{K})} = \ln(K_p)$$

$$e^{-\frac{70.54\,\frac{\text{kJ}}{\text{mol}}}{\left(8.314\,\frac{\text{J}}{\text{mol K}}\right)(298.15\,\text{K})}} = K_p$$

$$K_p \approx e^{-28.457} \approx 4.3776 \times 10^{-13}$$

Thus, the K_p value for $2\,\text{NO}_2(\text{g}) \rightleftharpoons 2\,\text{NO}(\text{g}) + \text{O}_2(\text{g})$ 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

$$\Delta G_{\text{rxn}} = \sum nG_f^\circ(\text{products}) - \sum nG_f^\circ(\text{reactants})$$

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:

$$C_2H_5OH(l) + O_2(g) \rightleftharpoons H_2O(l) + CO_2(g)$$

This reaction has an equilibrium constant of K_1. If you multiply this equation by 5, will the equilibrium constant change? If so, write this new equilibrium constant, K_2, in terms of K_1.

Solution

Because:

$$K = \frac{[A]^a[B]^b}{[C]^c[D]^d}$$

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,

$$C_2H_5OH(l) + 3\ O_2(g) \rightleftharpoons 3\ H_2O(l) + 2\ CO_2(g)$$

the corresponding equilibrium constant is

$$K_1 = \frac{[CO_2]^2}{[O_2]^3}$$

since liquid is ignored.

When we multiply this equation by 5, the chemical equation becomes,

$$5\,C_2H_5OH(l) + 15\,O_2(g) \rightleftharpoons 15\,H_2O(l) + 10\,CO_2(g)$$

the corresponding equilibrium constant is

$$K_2 = \frac{[CO_2]^{10}}{[O_2]^{15}} = \left(\frac{[CO_2]^2}{[O_2]^3}\right)^5$$

Therefore, for this reaction, the equilibrium constant changes and $K_2 = K_1^5$.

Q21

An unknown gas B_5D_{10} reacts at room temperature and becomes $B_{10}D_{20}$, the reaction is illustrated with the equation

$$2\,B_5D_{10}(g) \rightleftharpoons B_{10}D_{20}(g)$$

At room temperature the equilibrium partial pressure of B_5D_{10} is 1.23×10^{-4} atm and that of $B_{10}D_{20}$ is 3.14×10^{-16} atm. Given these constants, what is K_p of this reaction at room temperature.

Solution

Given that we already know the partial pressures and this reaction is at equilibrium, we simply substitute the values into the equilibrium equation and solve for K_p.

$$K_p = \frac{[\text{products}]}{[\text{reactants}]}$$

$$K_p = \frac{[3.14 \times 10^{-16}]}{[1.23 \times 10^{-4}]^2} = 2.08 \times 10^{-8}$$

$$K_p = 2.08 \times 10^{-8}$$

Q23A

Suppose there exists a compound that can be found in two forms, red and blue, such that

$$X_{red} \rightleftharpoons X_{blue}$$

During equilibrium at 25.0°C, 17% of the substance is determined to be in blue form. What is the equilibrium constant for this reaction?

Solution

The equilibrium constant, K_{eq}, for the chemical equation

$$X_{red} \rightleftharpoons X_{blue}$$

can be calculated by constructing the following equation:

$$K_{eq} = \frac{[X_{blue}]}{[X_{red}]}$$

Given that 17% of the concentration is X_{blue}, that means the remaining 83% is X_{red}, which can be plugged into the equation to yield

$$K_{eq} = \frac{[0.17]}{[0.83]} = 0.205$$

which can be further reinforced by viewing it as the fact that since $K_{eq} < 1$, the concentration of products present is expected to be smaller than the concentration of reactants.

Q23B

1,2-dimethylcyclohexane can exist in both boat and chair conformation. There is equilibrium between the two forms. What is the equilibrium constant for the reaction of boat conformation to chair conformation if the molecules in the boat form are 68.7%?

Solution

$$[\text{Boat}] \longrightarrow [\text{Chair}]$$

Let B stand for Boat and C stand for Chair, then the equilibrium constant for this reaction is

$$K = \frac{[\text{C}]}{[\text{B}]}$$

For [C] and [B] here, we can use the molar concentration $c = n/V$, then

$$[\text{C}] = n(\text{C})/V$$

$$[\text{B}] = n(\text{B})/V$$

So

$$K = \frac{n(\text{C})/V}{n(\text{B})/V} = \frac{n(\text{C})}{n(\text{B})} = \frac{n(\text{C})/n_{\text{tot}}}{n(\text{B})/n_{\text{tot}}}$$

From the question, it consists only with boat and chair conformation, so $n(\text{C})/n_{\text{tot}} = 0.687$, and the remaining is for boat, so $n(\text{B})/n_{\text{tot}} = 1 - 0.687 = 0.313$.

Therefore, the equilibrium constant is

$$K = \frac{n(\text{C})/n_{\text{tot}}}{n(\text{B})/n_{\text{tot}}} = \frac{0.687}{0.313} = 2.19$$

Q28

The K_p for the following reaction is 3.0 at 1000 K.

$$\text{CO}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons 2\,\text{CO}(\text{g})$$

a. If the pressure in the container where the reaction occurs was initially 0.48 bar, calculate the partial pressures of CO_2 and CO at equilibrium.
b. Calculate the percentage of CO_2 that has been dissociated.

Solution

a)

$$\text{CO}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons 2\,\text{CO}(\text{g})$$

	$\text{CO}_2(\text{g})$	$\text{CO}(\text{g})$
Initial	0.48	0
Change	$-x$	$+2x$
Equilibrium	$0.48 - x$	$2x$

$$K_p = \frac{p(\text{CO})^2}{p(\text{CO}_2)}$$

⇒

$$3 = \frac{(2x)^2}{(0.48 - x)}$$

⇒

$$4x^2 = 3(0.48 - x)$$

⇒

$$4x^2 = 1.44 - 3x$$

⇒

$$4x^2 + 3x - 1.44 = 0$$

By solving the quadratic equation, the positive value we get is

$$x = 0.33$$

Hence at equilibrium,

$$p(\mathrm{CO}) = 2x = 0.66$$

$$p(\mathrm{CO_2}) = 0.48 - x = 0.48 - 0.33 = 0.15 \text{ bar}$$

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	$\mathrm{XO_3}$	$\mathrm{O_2}$	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

$$\mathrm{F_2(g) + H_2(g) \rightleftharpoons 2\,HF(g)}$$

at 298 K is 5.07×10^4. Hydrogen with a partial pressure of 0.03500 atm is mixed with fluorine with a partial pressure of 0.06800 atm, and allowed to reach the equilibrium. What is the partial pressure of each of the gasses at the equilibrium?

Solution

We are looking for partial pressures of the reactants and we have starting partial pressures and a K_c value. First we need to convert K_c to K_p

$$K_p = K_c(RT)^{\Delta n_{gas}}$$

$$K_p = (5.07 \times 10^4) \times (0.0821 \times 298 \text{ K})^0 = 5.07 \times 10^4$$

The equilibrium constant can be constructed from the equation given

$$K_p = \frac{[HF]^2}{[H_2][F_2]}$$

Use an ICE table to find the equilibrium partial pressures of the equilibrium

Reaction	$\mathrm{H_2(g)}$	$\mathrm{F_2(g)}$	$\mathrm{2\,HF(g)}$
I	0.035	0.068	0
C	$-x$	$-x$	$+2x$
E	$0.035 - x$	$0.068 - x$	$2x$

$$5.07 \times 10^4 = \frac{[2x]^2}{[0.035 - x]^2[0.068 - x]^2}$$

Simplify the equation and solve as you wish. You can't use the quadratic formula because you end up with a degree three equation but you can put the equation into a graphing calculator and solve for x using the zero function.

$$x = 0.0286 \text{ atm}$$

$$[\mathrm{HF}] = 2x = 0.0571\ \mathrm{atm}$$

$$[\mathrm{H_2}] = 0.035 - x = 0.00643\ \mathrm{atm}$$

$$[\mathrm{F_2}] = 0.068 - x = 0.0394\ \mathrm{atm}$$

Q33

At 25 °C, the equilibrium constant for the reaction below has the value of 1.7×10^{-13}:

$$\mathrm{N_2O(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{NO(g)}$$

In a container where $\mathrm{N_2O}$ has an initial partial pressure of 0.62 atm, $\mathrm{O_2}$ has a pressure of 0.24 atm, and NO has an initial pressure of 0.08 atm, what will the partial pressure of the three gases be after reaching equilibrium at the same temperature?

Q35

The reaction:

$$2\,\mathrm{HI(g)} \rightleftharpoons \mathrm{H_2(g)} + \mathrm{I_2(g)}$$

has an equilibrium constant $K_c = 1.82 \times 10^{-2}$ at 698 K. If the reaction took place in a tank at 698 K and started off with HI having a partial pressure of 1 atm, what would the partial pressures of all the gases be at equilibrium?

Solution

First, we need to convert K_c into K_p with the equation

$$K_p = K_c(RT)^{\Delta n}$$

$$K_p = 1.82 \times 10^{-2}(0.0821\ \mathrm{L\ atm\ /\ K\ mol} \times 698\ \mathrm{K})^{2-2}$$

$$K_p = 1.82 \times 10^{-2}$$

An ICE table can also be constructed for the reaction:

$$2\,\mathrm{HI(g)} \rightleftharpoons \mathrm{H_2(g)} + \mathrm{I_2(g)}$$

ICE Table	$2\,\mathrm{HI(g)}$	$\mathrm{H_2(g)}$	$\mathrm{I_2(g)}$
Initial	1	0	0
Change	$-2x$	$+x$	$+x$
Equilibrium	$1-2x$	x	x

$$0.82 \times 10^{-2} = \frac{x^2}{1-2x}$$

$$x^2 = 1.82 \times 10^{-2} - 0.0368x$$

$$x = 0.118488$$

$$\text{partial pressure of HI} = 0.763\ \mathrm{atm}$$

$$\text{partial pressure of } \mathrm{H_2} = \text{partial pressure of } \mathrm{I_2} = 0.1189\ \mathrm{atm}$$

Q37

What is the concentration of a XY that will be found in equilibrium at room temperature, given that $\mathrm{X_2}$ 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

https://chem.libretexts.org/@go/page/531572

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.

$$2\,\mathrm{XY(g)} \rightleftharpoons \mathrm{X_2(g)} + \mathrm{Y_2(g)}$$

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$K_c = \frac{[\mathrm{X_2}][\mathrm{Y_2}]}{[\mathrm{XY}]^2} = \frac{[3.14 \times 10^{-15}][1.23 \times 10^{-4}]}{[\mathrm{XY}]^2} = 2.22 \times 10^{-7}$$

$$K_c = \frac{[3.86 \times 10^{-19}]}{[\mathrm{XY}]^2} = 2.22 \times 10^{-7}$$

$$K_c = 3.86 \times 10^{-19} = 2.22 \times 10^{-7}[\mathrm{XY}]^2$$

$$[\mathrm{XY}] = 1.32 \times 10^{-6}$$

So the concentration of XY is 1.32×10^{-6} M in equilibrium at 25ºC.

Q41

Hydrogen and oxygen gas react with each other to form gaseous water with an equilibrium constant for the reaction is $K_c = 1.33 \times 10^{20}$ 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)

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

$$K = 3.4 = \frac{1}{P_{\mathrm{H_2}}^2 P_{\mathrm{O_2}}}$$

$$P_{\mathrm{H_2}} = 1.2\ \mathrm{atm}$$

$$3.4 = \frac{1}{(1.2)^2 P_{\mathrm{O_2}}}$$

$$P_{\mathrm{O_2}} = \frac{1}{(1.2)^2(3.4)} = 0.204\ \mathrm{atm}$$

b) Excess $\mathrm{H_2O(l)}$ is added drive the reaction to the left towards the reactant to reach the equilibrium; therefore, pressure of H_2 and O_2 increased.

	$2\,\mathrm{H_2(g)}$	$\mathrm{O_2(g)}$	$2\,\mathrm{H_2O(l)}$
Initial	0	0.3	N/A
Change	$+2x$	$+x$	N/A
Equilibrium	$2x$	$0.3 + x$	N/A

$$K = \frac{1}{(2x)^2(0.3 + x)} = 3.4$$

$$3.4(0.3 + x)(2x)^2 = 1$$

$$x = 0.339\ \text{atm}$$

$$P_{O_2} = 0.3 + 0.339 = 0.639\ \text{atm}$$

$$P_{H_2} = 2(0.339) = 0.678\ \text{atm}$$

Q43

If you decompose ammonium nitrate into water and nitrous oxide, which further decomposes into oxygen and nitrogen gas, making the final reaction:

$$2\,NH_4NO_3(s) \rightleftharpoons 2\,N_2(g) + O_2(g) + 4\,H_2O(g)$$

This reaction takes place only in the molten salt, above its melting point of 169.6°C (for the anhydrous product). So, you get your 170°C blow torch and begin decomposing the ammonium nitrate under a sealed hood. Upon decomposition, all of the ammonium nitrate is gone, i.e. the reaction goes to completion.

a. What can be said of the equilibrium constant of this reaction at 170°C?
b. Now, in another universe, the partial pressure of $N_2(g)$ is 0.3 atm initially. Will the reaction still go to, essentially, completion?

Solution

(a) If there is no ammonium nitrate left, then the reaction was **heavily** products favoring, meaning K is extremely high at 170°C.

Note: It's more accurate to say that Q is a big number when there is no reactants left after reaction occurred. Reviewer's comment: Q stands for the current state. K is the equilibrium constant. When there is no reactant left after reaction occurred, the reaction is at the equilibrium state, so Q = K. Since Q is a big number, then K is also a big number.

(b) There would have to be an enormous amount of Nitrogen to force the reaction backwards. Because 0.3 atm is likely not enough to push back an essentially irreversible reaction, it has no noticeable affect on the amount of end product. (Note: If the reactants and products are essentially gas, we calculate the equilibrium constant not by its concentration, but by its pressure.)

Q45

Al_2Cl_6 at a partial pressure of 0.600 atm is placed in a closed container at 454 K. Al_3Cl_9 (partial pressure 1.98×10^{-3} atm) is also placed in it as well. Argon is added to raise the total pressure up to 1.00 atm.

Find whether if there is going to be net production or consumption of Al_3Cl_9 given $K_p = 1.04 \times 10^{-4}$. Then find the final pressure of Al_3Cl_9.

Solution

The reaction is

$$3\,Al_2Cl_6(g) \rightleftharpoons 2\,Al_3Cl_9(g)$$

Because argon does not react, it can be ignored.

$$Q = \frac{([Al_3Cl_9])^2}{([Al_2Cl_6])^3} = \frac{(1.98 \cdot 10^{-3})^2}{(0.600)^3} = 1.82 \cdot 10^{-5} < K_p = 1.04 \cdot 10^{-4}$$

There will be production of Al_3Cl_9.

ICE Table	Al_2Cl_6	Al_3Cl_9
Initial	0.600	1.98×10^{-3}
Change	$-3y$	$+2y$
Equilibrium	$0.6 - 3y$	$1.98 \times 10^{-3} + 2y$

$$K = 1.04 \cdot 10^{-4} \frac{([Al_3Cl_9])^2}{([Al_2Cl_6])^3} = \frac{(1.98 \times 10^{-3} + 2y)^2}{(1 - (1.98 \times 10^{-3} + 2y))^3}$$

Solving out

$$y = 0.0041 \text{ atm}$$

Al_3Cl_9 final pressure = 0.0102 atm.

Q46

The thermal decomposition of NH_4Cl solid proceeds as follows:

$$\mathrm{NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)}$$

the equilibrium constant at 275°C is 1.04×10^{-2}. If the partial pressures of $\mathrm{NH_3(g)}$ 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

$$P_{\mathrm{NH_3}} + P_{\mathrm{HCl}} = 0.200 \text{ atm}$$

The second equation is from the question that partial pressures of $\mathrm{NH_3(g)}$ and $\mathrm{HCl(g)}$ are equal

$$P_{\mathrm{NH_3}} = P_{\mathrm{HCl}}$$

Hence,

$$P_{\mathrm{NH_3}} = P_{\mathrm{HCl}} = 0.100 \text{ atm}$$

$$Q(\text{reaction quotient}) = P_{\mathrm{NH_3}} P_{\mathrm{HCl}} = (0.100)^2$$

$$10^{-2} < 1.04 \times 10^{-2}$$

$$Q < K$$

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.

$$\mathrm{2\,NO_2(g) \rightleftharpoons N_2O_4(g)}$$

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)

$$\mathrm{2\,NO_2(g) \rightleftharpoons N_2O_4(g)}$$

$$P_{\mathrm{N_2O_4}} = 0.59 \text{ atm} \quad P_{\mathrm{NO_2}} = 0.38 \text{ atm}$$

$$Q_p = \frac{P_{\mathrm{N_2O_4}}}{(P_{\mathrm{NO_2}})^2}$$

$$Q_p = \frac{0.59}{0.38^2} = 4.1$$

b) Since the mixture becomes more brown as the reaction reaches equilibrium, more NO gas is being produced, therefore the reverse reaction is favored, so $Q_p > k_p$, in conclusion, $K_p < 4.1$.

Q49

At 500 K the equilibrium constant for the reaction:

$$\mathrm{PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)}$$

is $K_{eq} = 2.1$. Suppose the equilibrium is disturbed and shifts, while temperature remains constant. Calculate the reaction quotient for each one of the possible changes in equilibrium concentration given below and evaluate in what direction the reaction will shift to reestablish equilibrium.

a. [PCl_3]= 0.0563, [Cl2]= 0.0784, [PCl_5]= 0.8934.
b. [PCl_3]=0.4390 , [Cl2]= 0.3547, [PCl_5]= 0.1048.
c. [PCl_3]= 0.4018, [Cl2]= 0.8690, [PCl_5]= 0.7205.

Q48

NO_2 has a brownish color. At elevated temperatures, NO_2 reacts with CO

$$\mathrm{NO_2(g) + CO(g) \rightleftharpoons NO(g) + CO_2(g)}$$

The other gases in this equation are colorless. When a gas mixture is prepared at 600K, in which 9.6 atm is the initial partial pressure of both NO_2 and CO, and 5.4 atm is the partial pressure of both NO and CO_2, the brown color of the mixture observed begins to get stronger as the reaction progresses toward equilibrium. Give a condition that must be satisfied by the equilibrium constant K.

Q51

The equilibrium constant (K_p) for the reaction

$$\mathrm{As_4(g) \rightleftharpoons 2\ As_2(g)}$$

is 5.5837×10^{-4} at 1090 K.

a. The initial molarity of $[\mathrm{As_4}]$ is 2.3 M and the initial molarity of $[\mathrm{As_2}]$ is 0.001 M. Calculate the reaction quotient Q and determine which way the reaction proceeds.
b. Calculate the molarity of each compound at the equilibrium.
c. Which direction will the reaction proceed if the pressure on the reaction decreases? Explain your answer.

Solution

(a) First, because you are given the initial molarities of your products and reactants and a Kp instead of a Kc value, you have to convert Kp to Kc using the formula:

$$K_p = K_c(RT)^{\Delta n_{\text{gas}}}$$

Plug in your given values

$$5.5837 \times 10^{-4} = K_c(0.0821 \times 1090)^{2-1} = 89.489K_c$$

$$K_c = 6.24 \times 10^{-6}$$

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	$2.3-x$	$0.001+2x$

$$6.24\times10^{-6}=\frac{[0.001+2x]^2}{[2.3-x]}$$

$$4x^2+0.00400624x-1.3352\times10^{-5}=0$$

Use the quadratic equation to find x

$$x=-0.0024,0.00139$$

-0.0024 is negative, which can't happen in real life so we know \(x) actually equals 0.00139.

[P_4]= 2.29861 M

[P_2]= 0.00378 M

(c) The reaction will progress towards the right because as pressure decreases, the reaction moves towards the side with the most moles of gas, which is the products.

Q55

Consider a reaction involving only gaseous compounds. The product yield at equilibrium decreases when the temperature and volume increase.

a. Is this reaction endothermic or exothermic?
b. Does the number of gas molecules in this reaction increase or decrease?

Solution

a. Exothermic. In exothermic reactions, product yield is indirectly related to temperature. In endothermic reactions, product yield is directly related to temperature. These properties can be further explained when heat is thought of as a reactant or a product. In exothermic reactions, heat is a product, and in endothermic reactions, heat is a reactant. When heat is added to a reaction, the equilibrium shifts to the opposite side to relieve stress on the system.

b. Decreases. The number of gas molecules is directly related to the volume of the container in which the reaction is happening. For example, if the volume of the container is decreased, the reaction will shift to whichever side has fewer moles of gas.

Q57

the Haber process, also called the Haber–Bosch process, is an artificial nitrogen fixation process and is the main industrial procedure for the production of ammonia today.

$$\mathrm{N_3+3\,H_2\rightleftharpoons 2\,NH_3}\quad(\Delta H=-92.4\,\mathrm{kJ/mol})$$

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:

$$PV = nRT \tag{13.E.1}$$

$$n = \frac{PV}{RT} = \frac{1\,\text{atm} \times 2.5\,\text{L}}{0.082 \frac{\text{L atm}}{\text{mol K}} \times 283.15\,\text{L}} = 0.1077\,\text{mol} \tag{13.E.2}$$

$$m_{CO_2} = n_{CO_2} \times \text{molar mass} = 0.1077\,\text{mol} \times 44\,\text{g/mol} = 4.7388\,\text{g} \tag{13.E.3}$$

$$m_{H_2O} = 500\,\text{g} - 4.7388\,\text{g} = 495.29\,\text{g} \tag{13.E.4}$$

$$n_{H_2O} = \frac{495.29\,\text{g}}{18\,\text{g/mol}} = 27.5\,\text{mol} \tag{13.E.5}$$

$$\text{Solubility of } \ce{CO2} \text{ in water} = \frac{0.1077\,\text{mol}}{0.5\,\text{kg}} = 0.2154\,\text{mol/kg} \tag{13.E.6}$$

Due to the Ideal gas law, the ratio of moles equals to the ratio of pressure

pressure: pressure = mol:mol = 0.1077: 27.51

because the total pressure is 2 atm, partial pressure of CO_2 = 0.0724 atm

Due to Henry's law:

$$k = \frac{c}{P} = \frac{0.2154 mol/kg}{0.0724\ atm} = 2.9751 \frac{mol}{kg\ atm} \tag{13.E.7}$$

Q61

The equilibrium constant for a reaction increases from $\text{K}=4 \cdot 5 \times 10^{-2}$ to $\text{K}=4 \cdot 5$ as the temperature increases from 0.00°C to 300.0°C. Assuming the change in enthalpy (ΔH) and change in entropy (ΔS) are constant over this range of temperatures, what is ΔS for this reaction? Is this reaction endothermic or exothermic?

Solution

Assuming ΔH and ΔS are constant, we can set up a system of equations as follows:

$$\begin{cases} \Delta G_{0.00^{\circ}\text{C}} = \Delta\text{H} - \text{T}\Delta\text{S} \\ \Delta G_{300.0^{\circ}\text{C}} = \Delta\text{H} - \text{T}\Delta\text{S} \end{cases}$$

We can determine $\Delta G_{0.00^{\circ}\text{C}}$ and $\Delta G_{300.0^{\circ}\text{C}}$ by utilizing the equation below that relates ΔG to K_{eq}:

$$\Delta G = -\text{RT}\ln(\text{K}) \quad \text{Easily remembered using the mnemonic: "}\Delta\text{Get in the }-\text{RighT lane, K?"}$$

$$\Delta G_{0.00^{\circ}\text{C}} = -\left(8.314 \frac{\text{J}}{\text{K} \times \text{mol}}\right)(273.15\text{K})\left(\ln(4.5 \times 10^{-2})\right) = 7042.5 \frac{\text{J}}{\text{mol}}$$

$$\Delta G_{300.0^{\circ}\text{C}} = -\left(8.314 \frac{\text{J}}{\text{K} \times \text{mol}}\right)(573.15\text{K})\left(\ln(4.5)\right) = -7167.2 \frac{\text{J}}{\text{mol}}$$

These values can then be plugged back into the original system of equations to obtain

$$\begin{cases} \Delta G_{0.00^{\circ}\text{C}} = 7042.5 \frac{\text{J}}{\text{mol}} = \Delta\text{H} - (273.15\text{K})\,\Delta\text{S} \\ \Delta G_{300.0^{\circ}\text{C}} = -7167.2 \frac{\text{J}}{\text{mol}} = \Delta\text{H} - (573.15\text{K})\,\Delta\text{S} \end{cases}$$

To calculate the values of the remaining two unknown variables, a substitution can be made that expresses ΔH in terms of ΔS.

$$-7167.2 \frac{\text{J}}{\text{mol}} + (573.15\text{K})\,\Delta\text{S} = \Delta\text{H}$$

This substitution can be plugged into the first equation to calculate the value for ΔS.

$$7042.5\,\tfrac{\text{J}}{\text{mol}} = -7167.2\,\tfrac{\text{J}}{\text{mol}} + (573.15\text{K})\,\Delta\text{S} - (273.15\text{K})\,\Delta\text{S}$$

$$\Delta\text{S} = 47.37\,\tfrac{\text{J}}{\text{K}\times\text{mol}}$$

ΔH can be calculated now by plugging in the value for ΔS into either one of the equations in the original set.

$$7042.5\,\tfrac{\text{J}}{\text{mol}} = \Delta\text{H} - (273.15\text{K})\left(47.37\,\tfrac{\text{J}}{\text{K}\times\text{mol}}\right)$$

$$\Delta\text{H} = 19980\,\tfrac{\text{J}}{\text{mol}} = 19.98\,\tfrac{\text{kJ}}{\text{mol}}$$

Because ΔH is positive, we know the reaction is endothermic.

Q63A

The equilibrium constant for the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\,\text{NO}_2(\text{g})$ is measured to be 5.9×10^{-3} at 298\;K and 1.3×10^{-6} at 398 K

a. Calculate ΔG° at 298 K for the reaction.
b. Calculate ΔH and ΔS°, assuming the enthalpy and entropy changes are independent of temperature between 298 K and 398 K.

Solution

a.Use the equation $\Delta G^\circ = -RT\ln K$

$\Delta G^\circ = -RT\ln K = (-8.3145\ \text{J K mol}^{-1}) \times (298\ \text{K})(\ln 5.9\times10^{-3}) = -1.29\times10^4\ \text{J mol}^{-1}$

For one mole of the reaction as written, ΔG° is -1290 kJ.

b. Use van't Hoff equation and the values of K at 298 K and at 398 K to obtain ΔH°. Then get ΔS° from ΔG° and the equation $\Delta G^\circ = -RT\ln K$

$\ln(\frac{1.3\times10^{-6}}{5.9\times10^{-3}}) = \frac{\Delta H^\circ}{8.3145\ \text{J K}^{-1}\,\text{mol}^{-1}}(\frac{1}{398\ K} - \frac{1}{298\ K})$

$\Delta\ H^\circ = 83.0\ kJ$

The answer equals both $\Delta\ H^\circ$ at 298 K and 398 K because it is assumed in the derivation of the van't Hoff equation that $\Delta\ H^\circ$ is independent of temperature. Next,

$\Delta\ S^\circ = \frac{\Delta\ H^\circ - \Delta\ G^\circ}{T} = \frac{83.0\times10^3\ J - (-1.29\times10^4\ J)}{298\ K} = 323\ J\ K^{-1}$

Q63B

For the reaction: $\text{Br}_2(\text{g}) \rightleftharpoons 2\,\text{Br}(\text{g})$, the equilibrium constant is 4.64×10^{-29} at 25ºC 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{ \Delta S}{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°:

$$ln\frac{K_{500}}{K_{298}} = -\frac{\Delta H^\circ}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$

=> 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.

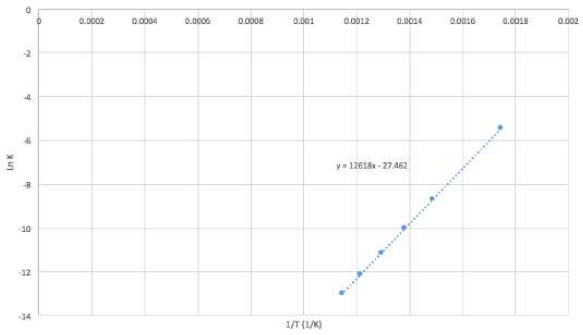
$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

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^o of the equilibrium reaction with ammonia? HINT: use the slope to find the ΔH^o

Solution

The graph bellow shows what the graph should look like:



First we must write the van't Hoff equation:

$$\ln K = -\frac{\Delta H^o}{R}\frac{1}{T} + \frac{\Delta S^o}{R}$$

Writing the equation like this how it can be compared with y = mx + b. With this information we then know that the slope of the graphe is equal to -ΔH^o/R. So:

$$\Delta H^o = \text{-mR were R = 8.3145 J K}^{-1}\text{mol}^{-1}$$

$$\Delta H^o = \text{-104.9 kJ mol}^{-1}$$

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 0.125Mas $\text{I}_2(\text{CCl}_4)$ 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 ($CaCO_3$) occurs according to the following reaction:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

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:

$$K_{eq} = p\mathrm{CO_2}] \tag{13.E.8}$$

Now we just need to plug in the pressure of CO_2: K_{eq} = [0.5] = 0.5

b. The total pressure would still be 0.5 atm because solids have an activity of 1 so they don't effect the equilibrium pressure.
c. The new equilibrium constant would be 1.0 atm.

Q87

Let's say you have the reaction:

$$A(s) + B(g) \leftrightharpoons C(s) + D(g)$$

At 25°C, this reaction has an equilibrium constant of 157.2. Find the partial pressures of $B(g)$ and $D(g)$ when the total pressure of the system is equal to 4.3 atm.

Solution

First, the equilibrium expression of this reaction is

$$K_c = \frac{D(g)}{B(g)} = 157.2$$

Note, the A(s) and C(s) are not included in this expression because they are solids. Solids have an activity equal to 1 which basically means they do not affect the equilibrium of the reaction.

To calculate the partial pressure of our unknowns, we can use Dalton's Law of partial pressures:

$$P_A = X_A P_{Total}$$

Since we are looking for the partial pressure of each of our gases, and we already have the total pressure of the system, we need to find the mole fraction of each of our gases. To find it, we can manipulate the above equilibrium expression to get:

$$D(g) = 157.2\ B(g)$$

Here, we see that at equilibrium, there are 157.2 molecules of $D(g)$ for every 1 molecule of $B(g)$

Now that we have the ratio of molecules in this reaction, we can construct workable mole fractions.

$$X_D = \frac{157.2}{1+157.2}$$
$$X_B = \frac{1}{1+157.2}$$

Finally, we can plug everything in to find our partial pressures.

$$P_D = \frac{157.2}{158.2} \times (4.3\ atm) = 4.27\ atm$$
$$P_B = \frac{1}{157.8} \times (4.3\ atm) = 0.027\ atm$$

Q91

Given the reaction

$$C_3H_5N(g) + 3\ H_2(g) \leftrightharpoons C_5H_{11}N(g)$$

whose equilibrium constant is solved by this equation

$$log_{10}(K) = -20.28 + \frac{10.56\ K}{T}$$

a. Solve for K when $T = 200\ K$
b. What is partial pressure of $C_3H_5N(g)$ when $T = 200\ K$ and the partial pressure of hydrogen is 1.0 atm and the partial pressure of $C_5H_{11}N(g)$ is 2.0×10^{-5} atm.

Solution

Part a)

$$log_{10}(K) = -20.28 + \frac{10.56\ K}{200\ K}$$

$$K = 10^{-20.23} = 5.89 \times 10^{-21}$$

part b)

Set up the equilibrium constant of the reaction, plug in your partial pressures, and solve for $C_3H_5N(g)$

$$K = \frac{[C_5H_{11}N]}{[C_5H_5N]\ [H_2]^3}$$

$$K = \frac{2.0 \times 10^{-5}}{[C_5H_5N]\ [1]}$$

$$[C_5H_5N] = 3.40 \times 10^{15}$$

Q93

Two equal volume solutions of 2M $HCOO^-$ and 2M HCOOH are mixed together. Assume that the volumes are additive. The value of the equilibrium constant Ka for HCOOH is 1.77 x 10^{-4}. What is the ratio between the amounts of HCOOH and $HCOO^-$ in the solution at equilibrium?

Solution

The chemical equation for this reaction is

$$HCOOH_{(aq)} + H_2O_l \leftrightarrow H_3O^+_{(aq)} + HCOO^-_{(aq)}$$

This indicates that

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

Because the volumes are equal and additive, the concentrations of the two solutions become half of what they were initially.

At equilibrium,

$$[HCOO^-] = 1 + x$$

$$[H_3O^+] = x$$

$$[HCOOH] = 1 - x$$

Plugging in these values into the equilibrium expression gives

$$1.77 \bullet 10^{-4} = \frac{[1+x][x]}{[1-x]}$$

Solving the equation for x gives

$$x = 1.77 \bullet 10^{-4} M$$

The ratio of HCOOH and $HCOO^-$ is

$$\frac{1+x}{1-x}$$

and due to x being such a small value, the ratio between the amounts of HCOOH and $HCOO^-$ is essentially 1.

Q101

The \(ΔG_f^o\) of $PbO(s)$ 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

$$PbO_{(s)} \rightleftharpoons Pb(s) + \frac{1}{2}O_2(g)$$

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

Q107

Calculate the pH of a 0.5 M H_3PO_4 acid solution given that $K_{a1} = 7.1 \times 10^{-3}$, $K_{a2} = 6.3 \times 10^{-8}$ and $K_{a3} = 4.2 \times 10^{-13}$.

Solution

A14.107V2

1.25

H14.107V2

Review on how to calculate the pH of a polyprotic acids here.

S14.107V2

$$7.1 \times 10^{-3} = \frac{x^2}{(0.5 - x)}$$

$$x = 0.0561\ M = [H^+]$$

$$pH = -\log[H^+] = 1.25$$

We assume that all of the H^+ in solution comes from the dissociation of the first H^+ because the second and the third is too small to have a significant effect in the pH of the solution.

Q107

The Haber-Bosch process is a method invented in the 20th century as a method for hydrogen fixation. It is widely used in industry today, and involves reacting nitrogen and hydrogen in the following manner:

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)}$$

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) $\Delta G° = -RT \ln(K)$

ΔG° = -(8.3145 J/K mol)(273 K) ln(60.2)

ΔG° = -9301.1 J/mol

b) ΔG = ΔG° + RT ln(Q)

ΔG = -9301.1 J/mol + (8.3145 J/K mol)(273 K) ln(P_{HI} / $P_{H2}P_{I2}$)

ΔG = -9301.1 J/mol + (8.3145 J/K mol)(273 K) ln(2 / (6x4))

ΔG = -14941.49 J/mol.

c) This reaction proceeds spontaneously in the forward direction.

Q109

At 773 K the equilibrium constant for the Haber-Bosch process is 1.45x10^{-5}. The chemical reaction involved in the Haber-Bosch process is:

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

a. What is $\Delta G^\circ(773)$ for this reaction?
b. What is ΔG at 773 K for transforming 1 mole of N_2 and 3 moles H_2 held at 30 atm to 2 moles of NH_3 held at 1 atm?
c. In which direction would the previous reaction run spontaneously?

Solution

a. The value of $\Delta G^\circ(773)$ can be found using the equation $\Delta G^\circ = -RT\ln K$ where T and K are already known to be 773 K and 1.45x10^{-5} respectively while R=8.134 J K^{-1} mol^{-1}.

$$\Delta G^\circ = -8.314\ J\ K^{-1}\ mol^{-1} \times 773K \times ln(1.45 \times 10^{-5}) = 70052\ J$$

$$\Delta G^\circ = 70052\ J$$

b. The equation needed to determine ΔG is $\Delta G = RTln(Q/K)$. The values of R, T, and K are known while Q is

$$Q = \frac{P_{NH_3}^2/P_{ref}}{(P_{N_2}/P_{ref})(P_{H_2}^3/P_{ref})}$$

P_{ref} =1 atm and the other pressures are stated in the question. So to find Q, the pressures have to be plugged into the equation

$$Q = \frac{(1)^2}{(20)(20)^3} = \frac{1}{160000} = 6.25 \times 10^{-6}$$

Now that the value of Q is known, ΔG can be found

$$\Delta G = -8.314\ J\ K^{-1}\ mol^{-1} \times 773K \times ln(\frac{6.25 \times 10^{-6}}{1.45 \times 10^{-5}}) = -5291\ J$$

$$\Delta G = -5291\ J$$

c. The previous reaction would run towards the products spontaneously because $\Delta G < 0$.

Q111

The following reaction is exothermic

$$\mathrm{SnO_2(s) + 2\,H_2(g) \rightarrow Sn(g) + 2\,H_2O(l)}$$

a. What is the equilibrium expression based on this chemical equation?
b. What happens to the reaction if more H_2 is added? SnO_2 is added into the system?
c. What effect would an increase in temperature have on the system?
d. What affect would an increase in pressure have on the system?

Solution

a. Add texts here. Do not delete this text first.K = [Sn] / [H_2] This is because solids are not included in the equilibrium expression
b. If H_2 were added, the reaction would shift right, towards the products, more Sn is produced. If SnO_2 were added, there would be no effect on the equilibrium because SnO_2 is not involve in the equilibrium process (K).
c. The reaction would shift towards the reactants. The reaction is exothermic, so heat is treated like a product.
d. An increase in pressure would shift the reaction towards the side that has less mole of gas. Therefore, in this reaction, an increased in pressure would shift the reaction to the right, more products are produced. Q111

Q112

Given the chemical reaction

$$\mathrm{SnO_2(s) \rightleftharpoons Sn(s) + O_2(g)}$$

a. Formulate the equilibrium expression using activities
b. State the effect on $p\mathrm{O_2}$ at equilibrium if more $\mathrm{SnCl_4(l)}$ is added to the system
c. State the effect on $p\mathrm{O_2}$ at equilibrium if more $\mathrm{O_2(g)}$ is added to the system

Solution

a. The activities of solids and liquids are always equal to 1. The activities of gases are equal to the partial pressure of the gas in bars. Therefore the equilibrium expression would be

$$K = P_{O_2}$$

b. P_{O_2} would not change because the activity of a liquid is always 1 meaning it has no effect on the equilibrium constant

c. P_{O_2} would decrease because the extra gas would push the system out of equilibrium and in order for the system to return to equilibrium, some of the O_2 gas would have to react with some of the $Sn_{(s)}$. This would decrease the amount of $O_{2(g)}$ present in the system and therefore decrease the the pressure of $O_{2(g)}$.

Q113

Arrange the following solutions in order of most acidic to basic: NaOH, NaCN, H_2SO_4, NH_4NO_3, NaCl

Solution

$$\mathrm{H_2SO_4 > NH_4NO_3 > NaCl > NaCN > NaOH} \tag{13.E.9}$$

Review acids bases here.

- H_2SO_4 is a strong acid.
- NH_4NO_3 is formed by a weak base (NH_4OH) and a strong acid (HNO_3). Hence, NH_4NO_3 is acidic.
- NaCl is formed by a strong base (NaOH) and a strong acid (HCl). Hence, it is a neutral salt.
- NaCN is formed by a strong base (NaOH) and a weak acid (HCN). Hence, NaCN is basic.
- NaOH is a strong base.

Q115

Given that the K_b values for $\mathrm{NH_3}$ and $\mathrm{NH_2NH_2}$ are 1.8×10^{-5} and 8.5×10^{-7}, respectively. Which is the stronger acid?

Solution

$$\mathrm{NH_2NH_2}$$

Calculate the K_a values first. Review on how to identify the strength of an acid from its K_a value here.

For NH_3,

$$K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

For NH_2NH_2,

$$K_a = \frac{(1.0 \times 10^{-14}}{8.5 \times 10^{-7}} = 1.18 \times 10^{-8}$$

Since the Ka value of NH_2NH_2 is larger, NH_2NH_2 is the stronger acid.

Q119

Calculate the pH of the following solutions.

a. 0.5 M NaCN (K_a of $HCN = 6.2 \times 10^{-10}$)
b. 0.01 M NH_4Cl (K_b of $NH_3 = 1.8 \times 10^{-5}$)

Solution

11.5 5.63

Ka=(1*10^{-14})/(1.8*10^{-5})=5.56*10^{-10}
5.56*10^{-10}=x^2/(0.01-x)
x=2.36*10^{-6}
pH= -log(x)= 5.63

H14.119V2

Review on the properties of salts here.

\[\ce{CN^- (aq) + H2O (l) <=> HCN (aq) + OH^- (aq)}\]

Kb=(1*10^{-14})/(6.2*10^{-10})=1.62*10^{-5}

$$1.62 \times 10^{-5} = \frac{x^2}{0.5 - x} \tag{13.E.10}$$

x=0.00283

pOH= -log(x)= 2.55

pH= 14-pOH= 11.5

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \tag{13.E.11}$$

Q131

Identify the stronger acid in each of the following combination. Explain.

a. HF and HBr
b. H_2SO_4 and H_2SO_3
c. HOCl and HOBr

Solution

14.131V2

HBr H_2SO_4 HOCl

Study the effect of structure on acids and bases.

S14.131V2

1. HBr is the stronger acid because Br less electronegative and therefore less polar as compared to HF.
2. H_2SO_4 is the stronger acid because as the number of attached oxygen on the O-H bonds increases, the less polar the molecule is.
3. For oxyacids, the less polar oxyacids are the ones that are more electronegative. Since Cl is more electronegative than Br, HOCl is the stronger acid.

Q137

Identify the Lewis acid and Lewis base for each of the following reaction.

a. $H^+(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq)$
b. $Al^{3+}(aq) + 6\,H_2O(l) \rightleftharpoons Al(H_2O)_6^{3+}(aq)$
c. $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

Solution

	Lewis acid	Lewis base
1.	H^+	NH_3
2.	Al^{3+}	H_2O
3.	CO_2	H_2O

H14.137V2

Study the concept of electron pairs here.

S14.137V2

H^+ is the electron-pair acceptor while NH_3 is the electron-pair donor. Al^{3+} is the electron-pair acceptor while H_2O is the electron-pair donor. CO_2 is the electron-pair acceptor while H_2O is the electron-pair donor.

Q139

Beryllium hydroxide is an amphoteric compound. It can react as an acid as well as a base. Please write the reactions of $Be(OH)_2$ and describe its role base on Brønsted-Lowry and Lewis theories.

Solution

$Be(OH)_2(s)+2H^+(aq)$-> $Be^{2+}(aq)+2H_2O(l)$ (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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CHAPTER OVERVIEW

14: Acid–Base Equilibria

An General Chemistry Libretexts Textmap organized around the textbook

Principles of Modern Chemistry

by Oxtoby, Gillis, and Campion

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

Template:HideTOC

Acids and bases have been defined differently by three sets of theories. One is the Arrhenius definition, which revolves around the idea that acids are substances that ionize (break off) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide (OH^-) ions in solution. On the other hand, the Bronsted-Lowry definition defines acids as substances that donate protons (H^+) whereas bases are substances that accept protons. Also, the Lewis theory of acids and bases states that acids are electron pair acceptors while bases are electron pair donors. Acids and bases can be defined by their physical and chemical observations.

14.1: Classifications of Acids and Bases
14.2: Properties of Acids and Bases in Aqueous Solutions
14.3: Acid and Base Strength
14.4: Equilibria Involving Weak Acids and Bases
14.5: Buffer Solutions
14.6: Acid-Base Titration Curves
14.7: Polyprotic Acids
14.8: Organic Acids and Bases - Structure and Reactivity
14.9: A Deeper Look - Exact Treatment of Acid-Base Equilibria
14.10: Precipitation and Dissolution
14.E: Acid-Base Equilibria (Exercises)

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14.1: 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 14.1.1).

Table 14.1.1: General Properties of Acids and Bases

ACIDS	BASES
produce a piercing pain in a wound.	give a slippery feel.
taste sour.	taste bitter.
are colorless when placed in phenolphthalein (an indicator).	are pink when placed in phenolphthalein (an indicator).
are red on blue litmus paper (a pH indicator).	are blue on red litmus paper (a pH indicator).
have a pH<7.	have a pH>7.
produce hydrogen gas when reacted with metals.	
produce carbon dioxide when reacted with carbonates.	
Common examples: Lemons, oranges, vinegar, urine, sulfuric acid, hydrochloric acid	Common Examples: Soap, toothpaste, bleach, cleaning agents, limewater, ammonia water, sodium hydroxide.

Acids and bases in aqueous solutions will conduct electricity because they contain dissolved ions. Therefore, acids and bases are *electrolytes*. Strong acids and bases will be strong **electrolytes**. Weak acids and bases will be weak electrolytes. This affects the amount of conductivity.

In chemistry, acids and bases have been defined differently by **three sets of theories**: One is the Arrhenius definition defined above, which revolves around the idea that acids are substances that ionize (break off) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide (OH^-) ions in solution. The other two definitions are discussed in detail include the **Brønsted-Lowry definition** the defines acids as substances that donate protons (H^+) whereas bases are substances that accept protons and the **Lewis theory** of acids and bases states that acids are electron pair acceptors while bases are electron pair donors.

Arrhenius Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. The Arrhenius definition of acid-base reactions is a development of the "hydrogen theory of acids". It was used to provide a modern definition of acids and bases, and followed from Arrhenius's work with Friedrich Wilhelm Ostwald in establishing the presence of ions in aqueous solution in 1884. This led to Arrhenius receiving the Nobel Prize in Chemistry in 1903.

An **Arrhenius acid** is a compound that increases the concentration of H^+ ions that are present when added to water.

$$HCl(g) \rightarrow H^+(aq) + Cl^-(aq) \tag{14.1.1}$$

In this reaction, hydrochloric acid (HCl) gas dissociates into hydrogen (H^+) and chloride (Cl^-) ions when dissolved in water, thereby releasing H^+ ions into solution. These H^+ ions form the hydronium ion (H_3O^+) when they combine with water molecules. Both processes can be represented in a chemical equation by adding H_2O to the reactants side of Equation 14.1.1 and switching hydronium ions for free protons.

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{14.1.2}$$

An **Arrhenius base** is a compound that dissociates to yield hydroxide ions (OH^-) in aqueous solution. Common examples of Arrhenus bases include Sodium hydroxide ($NaOH$), Potassium hydroxide (KOH), Magnesium hydroxide $Mg(OH)_2$, and Calcium hydroxide ($Ca(OH)_2$. All of these bases are solids at room temperature and when dissolved in water, will generate a metal cation and the hydroxide ion ((OH^-), for example, Sodium hydroxide

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq) \tag{14.1.3}$$

All Arrhenius acids have easily detachable hydrogen that leave to form hydronium ions in solution and all Arrhenius bases have easily detachable OH groups that form hydroxide ions in solution.

Limitation of the Arrhenius Definition of Acids and Bases

The Arrhenius definitions of acidity and alkalinity are restricted to aqueous solutions and refer to the concentration of the solvated ions. Under this definition, pure H_2SO_4 or HCl dissolved in toluene are not acidic, despite the fact that both of these acids will donate a proton to toluene. In addition, under the Arrhenius definition, a solution of sodium amide ($NaNH_2$) in liquid ammonia is not alkaline, despite the fact that the amide ion (NH_2^-) will readily deprotonate ammonia. Thus, the Arrhenius definition can only describe acids and bases in an aqueous environment. The Arrhenius definition can **only** describe acids and bases in protic solvents and environments (e.g., water, alcohols, within proteins etc.).

Brønsted-Lowry Acids and Bases

The Arrhenius definitions identified an acid as a compound that dissolves in water to yield hydronium ions (Equation 14.1.2) and a base as a compound that dissolves in water to yield hydroxide ions (Equation 14.1.3). As mentioned above, this definition limited. We extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H^+. A proton is what remains when a normal hydrogen atom, ^1_1H, loses an electron. A compound that donates a proton to another compound is called a **Brønsted-Lowry acid**, and a compound that accepts a proton is called a **Brønsted-Lowry base**. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base).

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O. Anions (such as HSO_4^-, $H_2PO_4^-$, HS^-, and HCO_3^-) and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_6]^{3+}$) may also act as acids.

Bases fall into the same three categories and may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as $NaOH$ and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$H^+ + OH^- \rightarrow H_2O \tag{14.1.4}$$

We call the product that remains after an acid donates a proton the **conjugate base** of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base}$$

$$\ce{HF} \rightleftharpoons \ce{H^+} + \ce{F^-}$$

$$\ce{H_2SO_4} \rightleftharpoons \ce{H^+} + \ce{HSO_4^-}$$

$$\ce{H_2O} \rightleftharpoons \ce{H^+} + \ce{OH^-}$$

$$\ce{HSO_4^-} \rightleftharpoons \ce{H^+} + \ce{SO_4^{2-}}$$

$$\ce{NH_4^+} \rightleftharpoons \ce{H^+} + \ce{NH_3}$$

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):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid}$$

$$\ce{OH^-} + \ce{H^+} \rightleftharpoons \ce{H_2O}$$

$$\ce{H_2O} + \ce{H^+} \rightleftharpoons \ce{H_3O^+}$$

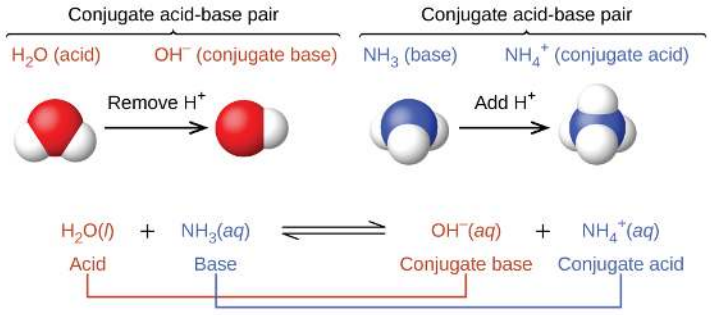
$$\ce{NH_3} + \ce{H^+} \rightleftharpoons \ce{NH_4^+}$$

$$\ce{S^{2-}} + \ce{H^+} \rightleftharpoons \ce{HS^-}$$

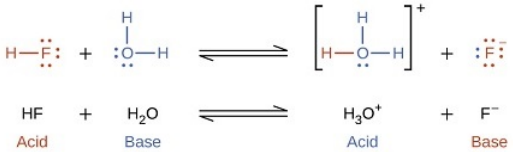
$$\ce{CO_3^{2-}} + \ce{H^+} \rightleftharpoons \ce{HCO_3^-}$$

$$\ce{F^-} + \ce{H^+} \rightleftharpoons \ce{HF}$$

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, $\ce{OH^-}$, and the conjugate acid of ammonia, $\ce{NH_4^+}$:



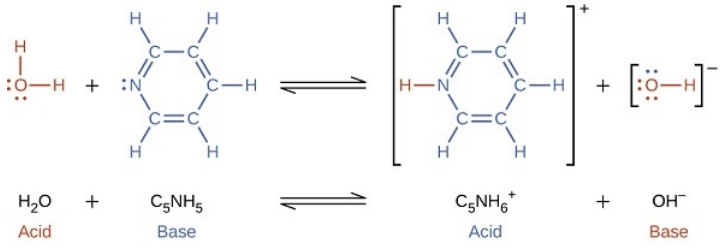
The reaction between a Brønsted-Lowry acid and water is called acid ionization. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



with

$$K = \frac{[\ce{H_3O^+}][\ce{F^-}]}{[\ce{HF}]}$$

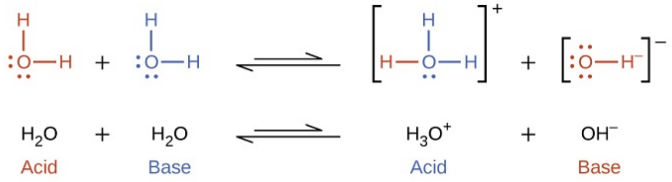
When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding ammonia to water yields hydroxide ions and ammonium ions:



with

$$K = \frac{[C_5NH_6^+][OH^-]}{[C_5NH_5]}$$

Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{14.1.5}$$

with

$$K_w = [H_3O^+][OH^-] \tag{14.1.6}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is approximately 5.1×10^{-13}, roughly 100-times larger than the value at 25 °C.

Example 14.1.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-]$. At 25 °C:

$$\begin{aligned} K_w &= [H_3O^+][OH^-] \\ &= [H_3O^+]^2 \\ &= [OH^-]^2 \\ &= 1.0 \times 10^{-14} \end{aligned}$$

So

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

? Exercise 14.1.1

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. Example 14.1.2 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

✓ Example 14.1.2: 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 14.1.2

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:

$$\mathrm{HCO{-}3\,(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)}$$

$$\mathrm{HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)}$$

Example 14.1.3: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of $\mathrm{HSO_3^-}$

a. as an acid with $\mathrm{OH^-}$
b. as a base with HI

Solution

a. $\mathrm{HSO_3^-}(aq) + \mathrm{OH^-}(aq) \rightleftharpoons \mathrm{SO_3^{2-}}(aq) + \mathrm{H_2O}_{(l)}$
b. $\mathrm{HSO_3^-}(aq) + \mathrm{HI}(aq) \rightleftharpoons \mathrm{H_2SO_3}(aq) + \mathrm{I^-}(aq)$

Exercise 14.1.3

Write separate equations representing the reaction of $\mathrm{H_2PO_4^-}$

a. as a base with HBr
b. as an acid with $\mathrm{OH^-}$

Answer a

$\mathrm{H_2PO_4^-}(aq) + \mathrm{HBr}(aq) \rightleftharpoons \mathrm{H_3PO_4}(aq) + \mathrm{Br^-}(aq)$

Answer b

$\mathrm{H_2PO_4^-}(aq) + \mathrm{OH^-}(aq) \rightleftharpoons \mathrm{HPO_4^{2-}}(aq) + \mathrm{H_2O}_{(l)}$

Lewis Acids and Bases

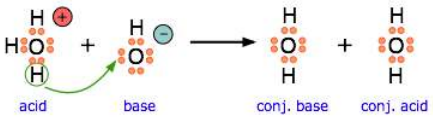
The Brønsted-Lowry proton donor-acceptor concept has been one of the most successful theories of Chemistry. But as with any such theory, it is fair to ask if this is not just a special case of a more general theory that could encompass an even broader range of chemical science. In 1916, G.N. Lewis of the University of California proposed that the *electron pair* is the dominant actor in acid-base chemistry. The Lewis theory did not become very well known until about 1923 (the same year that Brønsted and Lowry published their work), but since then it has been recognized as a very powerful tool for describing chemical reactions of widely different kinds and is widely used in organic and inorganic chemistry. The Brønsted–Lowry concept of acids and bases defines a base as any species that can accept a proton, and an acid as any substance that can donate a proton. Lewis proposed an alternative definition that focuses on *pairs of electrons* instead. According to Lewis:

- An *acid* is a substance that **accepts** a pair of electrons, and in doing so, forms a covalent bond with the entity that supplies the electrons.
- A *base* is a substance that **donates** an unshared pair of electrons to a recipient species with which the electrons can be shared.

> *In modern chemistry, electron donors are often referred to as nucleophiles, while acceptors are electrophiles.*

Lewis Acid-Base Neutralization Involving Electron-Pair Transfer

Just as any Arrhenius acid is also a Brønsted acid, any Brønsted acid is also a Lewis acid, so the various acid-base concepts are all "upward compatible". Although we do not really need to think about electron-pair transfers when we deal with ordinary aqueous-solution acid-base reactions, it is important to understand that it is the opportunity for electron-pair sharing that enables proton transfer to take place.



This equation for a simple acid-base neutralization shows how the Brønsted and Lewis definitions are really just different views of the same process. Take special note of the following points:

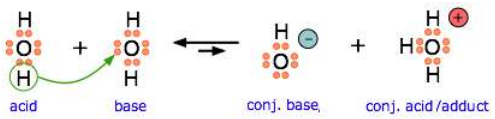
- The arrow shows the movement of a proton from the hydronium ion to the hydroxide ion.
- Note that the electron-pairs themselves do not move; they remain attached to their central atoms. The electron pair on the base is "donated" to the acceptor (the proton) only in the sense that it ends up being *shared* with the acceptor, rather than being the exclusive property of the oxygen atom in the hydroxide ion.
- Although the hydronium ion is the nominal Lewis acid here, it does not itself accept an electron pair, but acts merely as the source of the proton that coordinates with the Lewis base.

Note

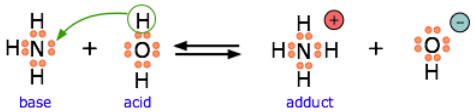
The point about the electron-pair remaining on the donor species is especially important to bear in mind. For one thing, it distinguishes a *Lewis acid-base reaction* from an *oxidation-reduction reaction*, in which a physical transfer of one or more electrons from donor to acceptor does occur.

The product of a Lewis acid-base reaction is known formally as an "**adduct**" or "complex", although we do not ordinarily use these terms for simple proton-transfer reactions such as the one in the above example. Here, the proton combines with the hydroxide ion to form the "adduct" H_2O. The following examples illustrate these points for some other proton-transfer reactions that you should already be familiar with.

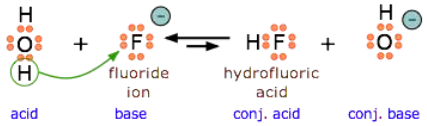
Another example, showing the autoprotolysis of water. Note that the conjugate acid is also the adduct.



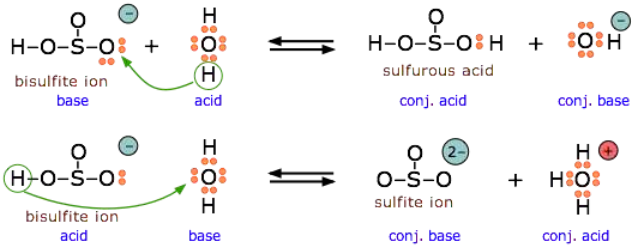
Ammonia is both a Brønsted and a Lewis base, owing to the unshared electron pair on the nitrogen. The reverse of this reaction represents the *hydrolysis* of the ammonium ion.



Because HF is a weak acid, fluoride salts behave as bases in aqueous solution. As a Lewis base, F^- accepts a proton from water, which is transformed into a hydroxide ion.



The bisulfite ion is *amphiprotic* and can act as an electron donor or acceptor.



All Brønsted–Lowry bases (proton acceptors), such as OH^-, H_2O, and NH_3, are also electron-pair donors. Thus the Lewis definition of acids and bases does not contradict the Brønsted–Lowry definition. Rather, it expands the definition of acids to include substances other than the H^+ ion.

Lewis Acid-Base Neutralization without Transferring Protons

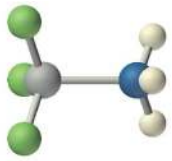
Electron-deficient molecules, such as BCl_3, contain less than an octet of electrons around one atom and have a strong tendency to gain an additional pair of electrons by reacting with substances that possess a lone pair of electrons. Lewis's definition, which is less restrictive than either the Brønsted–Lowry or the Arrhenius definition, grew out of his observation of this tendency. A general Brønsted–Lowry acid–base reaction can be depicted in Lewis electron symbols as follows:

$$\underset{\substack{\text{Lewis acid}\\ \text{Electron-pair}\\ \text{acceptor}}}{H^+} + \underset{\substack{\text{Lewis base}\\ \text{Electron-pair}\\ \text{donor}}}{:B} \longrightarrow H:B^+$$

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):

$$\underset{\text{Lewis acid}}{BF_3} + \underset{\text{Lewis base}}{:NH_3} \longrightarrow \underset{\text{Acid-base adduct}}{F_3B:NH_3}$$

The bond formed between a Lewis acid and a Lewis base is a **coordinate covalent bond** because both electrons are provided by only one of the atoms (N, in the case of $F_3B:NH_3$). After it is formed, however, a coordinate covalent bond behaves like any other covalent single bond.



Boron trifluoride-ammonia adduct

Species that are very weak Brønsted–Lowry bases can be relatively strong Lewis bases. For example, many of the group 13 trihalides are highly soluble in ethers (R–O–R′) because the oxygen atom in the ether contains two lone pairs of electrons, just as in H_2O. Hence the predominant species in solutions of electron-deficient trihalides in ether solvents is a Lewis acid–base adduct. A reaction of this type is shown in Figure 14.1.1 for boron trichloride and diethyl ether:

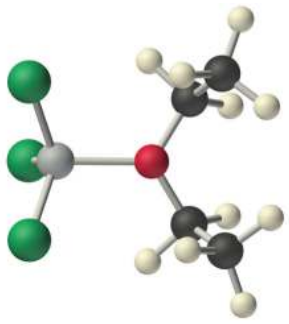
$$\underset{\text{Lewis acid}}{BCl_3} + \underset{\text{Lewis base}}{:\ddot{O}(CH_2CH_3)_2} \longrightarrow \underset{\text{Acid-base adduct}}{Cl_3B:\ddot{O}(CH_2CH_3)_2}$$

Figure 14.1.1: 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 14.1.2: 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.

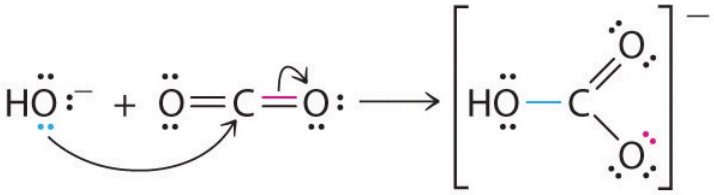


Figure 14.1.2 Lewis Acid/Base reaction of the hydroxide ion with carbon dioxide

Example 14.1.4

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 14.1.4A

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 14.1.4B

Here are several more examples of Lewis acid-base reactions that **cannot** be accommodated within the Brønsted or Arrhenius models. Identify the Lewis acid and Lewis base in each reaction.

a. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$
b. $SnS_2 + S^{2-} \rightarrow SnS_3^{2-}$
c. $Cd(CN)_2 + 2CN^- \rightarrow Cd(CN)_4^{2+}$
d. $AgCl + 2NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$
e. $Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$
f. $[Ni^{2+} + 6NH_3 \rightarrow Ni(NH_3)_5^{2+}$



Video 14.1.1: Overview of Lewis Acids and Bases

Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25\,^\circ C$$

Glossary

acid ionization

reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic

species that may either gain or lose a proton in a reaction

amphoteric

species that can act as either an acid or a base

autoionization

reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization

reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid

proton donor

Brønsted-Lowry base

proton acceptor

conjugate acid

substance formed when a base gains a proton

conjugate base

substance formed when an acid loses a proton

ion-product constant for water (K_w)

equilibrium constant for the autoionization of water

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14.2: Properties of Acids and Bases in Aqueous Solutions

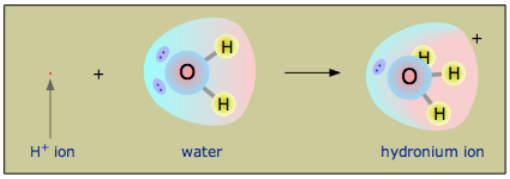
Learning Objectives

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- To know the relationship between acid or base strength and the magnitude of K_a, K_b, pK_a, and pK_b.
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

We now turn our attention to acid–base reactions to see how the concepts of chemical equilibrium and equilibrium constants can deepen our understanding of this kind of chemical behavior. We begin with a qualitative description of acid–base equilibria in terms of the Brønsted–Lowry model and then proceed to a quantitative description the following sections.

Free Hydrogen Ions do not Exist in Water

Owing to the overwhelming excess of H_2O molecules in aqueous solutions, a bare hydrogen ion has no chance of surviving in water. The hydrogen ion in aqueous solution is no more than a proton, a bare nucleus. Although it carries only a single unit of positive charge, this charge is concentrated into a volume of space that is only about a hundred-millionth as large as the volume occupied by the smallest atom. (Think of a pebble sitting in the middle of a sports stadium!) The resulting extraordinarily high *charge density* of the proton strongly attracts it to any part of a nearby atom or molecule in which there is an excess of negative charge. In the case of water, this will be the lone pair (unshared) electrons of the oxygen atom; the tiny proton will be buried within the lone pair and will form a shared-electron (coordinate) bond with it, creating a *hydronium ion*, H_3O^+. In a sense, H_2O is acting as a base here, and the product H_3O^+ is the conjugate acid of water:



Although other kinds of dissolved ions have water molecules bound to them more or less tightly, the interaction between H^+ and H_2O is so strong that writing "$H^+(aq)$" hardly does it justice, although it is formally correct. The formula H_3O^+ more adequately conveys the sense that it is both a molecule in its own right, and is also the conjugate acid of water. However, the equation

$$HA \rightarrow H^+ + A^-$$

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.

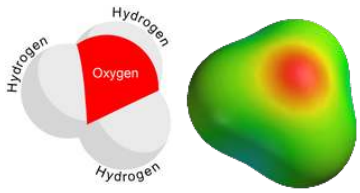


Figure 14.2.1. The picture above illustrates the electron density of hydronium. The red area represents oxygen; this is the area where the electrostatic potential is the highest and the electrons are most dense.

As H^+ ions are formed, they bond with H_2O molecules in the solution to form H_3O^+ (the hydronium ion). This is because hydrogen ions do not exist in aqueous solutions, but take the form the hydronium ion, H_3O^+. A reversible reaction is one in which the reaction goes both ways. In other words, the water molecules dissociate while the OH^- ions combine with the H^+ ions to form water. Water has the ability to attract H^+ ions because it is a polar molecule. This means that it has a partial charge, in this case the charge is negative. The partial charge is caused by the fact that oxygen is more electronegative than hydrogen. This means that in the bond between hydrogen and oxygen, oxygen "pulls" harder on the shared electrons thus causing a partial negative charge on the molecule and causing it to be attracted to the positive charge of H^+ to form **hydronium**. Another way to describe why the water molecule is considered polar is through the concept of dipole moment. The electron geometry of water is tetrahedral and the molecular geometry is bent. This bent geometry is asymmetrical, which causes the molecule to be polar and have a dipole moment, resulting in a partial charge.

The pH Scale

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is neutral if it contains equal concentrations of hydronium and hydroxide ions; acidic if it contains a greater concentration of hydronium ions than hydroxide ions; and basic if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities, the values of which may span many orders of magnitude, is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$\mathrm{pX} = -\log \mathrm{X} \tag{14.2.1}$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \tag{14.2.2}$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} \tag{14.2.3}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] \tag{14.2.4}$$

or

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}} \tag{14.2.5}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$\begin{aligned} K_\mathrm{w} &= [\mathrm{H_3O^+}][\mathrm{OH^-}] \\ -\log K_\mathrm{w} &= -\log([H_3O^+][OH^-]) \\ &= -\log[H_3O^+] + -\log[OH^-] \\ pK_w &= pH + pOH \end{aligned}$$

At 25 °C, the value of K_w is 1.0×10^{-14} and so:

$$14.00 = \text{pH} + \text{pOH} \tag{14.2.6}$$

The hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7}\ M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{14.2.7}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{14.2.8}$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities less than $1.0 \times 10^{-7}\ M$ (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7}\ M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the hydronium molarity of pure water at 80 °C is 4.9 × 10^{-7} M, which corresponds to pH and pOH values of:

$$\begin{aligned}\text{pH} &= -\log[H_3O^+] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \\ \text{pOH} &= -\log[OH^-] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31\end{aligned}$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table 14.2.1).

Table 14.2.1: 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 14.2.2 shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH, and gives values for these properties at standard temperatures for some common substances.

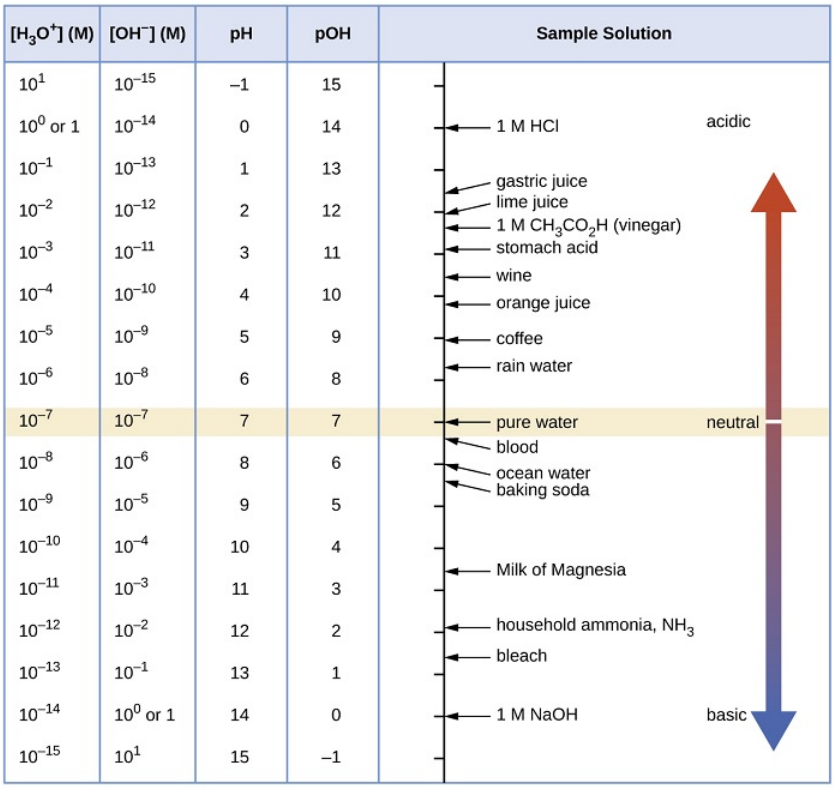


Figure 14.2.2: The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

Example 14.2.1: 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 14.2.1

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$$

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 14.2.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3.

Solution

$$\begin{aligned} \text{pH} = -\log[\text{H}_3\text{O}^+] &= 7.3 \\ [\text{H}_3\text{O}^+] &= 10^{-7.3} \\ [\text{H}_3\text{O}^+] &= 5 \times 10^{-8}\ M \end{aligned}$$

(On a calculator take the antilog, or the "inverse" log, of −7.3, or calculate $10^{-7.3}$.)

Exercise 14.2.2A

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Answer

12 M

This uses the definition of pH that we commonly use:

$$pH = -\log[H_3O^+]$$

So for this solution:

$$\begin{aligned} \text{pH} = -\log[\text{H}_3\text{O}^+] &= -1.07 \\ [\text{H}_3\text{O}^+] &= 10^{+1.07} \\ &= 12 \text{ (with significant figure)} \end{aligned}$$

However, at this high concentration, the solution will be non-ideal and we have to use the proper definition in terms of hydronium activities

$$pH = -\log a\{H_3O^+\}$$

See this module for more details.

Exercise 14.2.2B

The ionization constant of water Kw at 37 °C is 2.42×10^{-14}. What is the pH for a neutral solution at this human physiological temperature? Is the water acidic, basic or neutral?

Answer

$$\text{Kw} = [\text{H}_3\text{O}^+][\text{OH}^-] = 2.42 \times 10^{-14}$$

and

$$\begin{aligned} [\text{H}_3\text{O}^+] = [\text{OH}^-] &= \sqrt{2.42 \times 10^{-14}} \\ &= 1.55 \times 10^{-7} \end{aligned}$$

$$pH = -\log[H_3O^+] = -\log 1.55 \times 10^{-7} = 6.81 \tag{14.2.9}$$

If we use the definition of acidic systems like in Figure 14.2.2 then we would (incorrectly) argue the solution is acidic. However, since $[\text{OH}^-] = [\text{H}_3\text{O}^+]$, the solution is still neutral. This is only a strange idea, if one ignores the temperature dependence of Kw.

Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$\text{H}_2\text{O}_{(l)} + \text{CO}_{2(g)} \longrightarrow \text{H}_2\text{CO}_{3(aq)} \tag{14.2.10}$$

$$\text{H}_2\text{CO}_{3(aq)} \rightleftharpoons \text{H}^+_{(aq)} + \text{HCO}^-_{3(aq)} \tag{14.2.11}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2O_{(l)} + SO_{3(g)} \longrightarrow H_2SO_{4(aq)} \tag{14.2.12}$$

$$H_2SO_{4(aq)} \longrightarrow H^+_{(aq)} + HSO^-_{4(aq)} \tag{14.2.13}$$

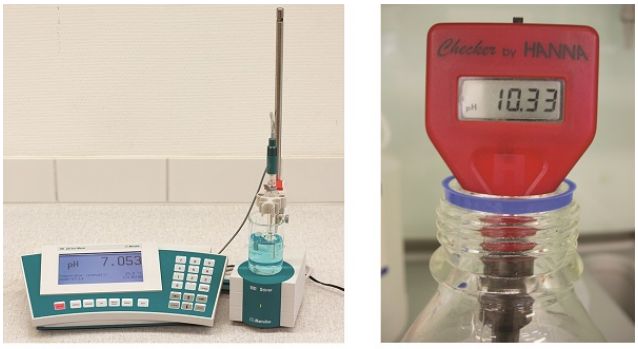
Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.


(a) (b)

Figure 14.2.3: (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 14.2.3). 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 14.2.4).



(a) (b)

Figure 14.2.4: (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 14.2.3: 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:

$$\text{pOH} = -\log[\text{OH}^-] = -\log 0.0125 \tag{14.2.14}$$

$$= -(-1.903) = 1.903 \tag{14.2.15}$$

The pH can be found from the pOH:

$$\text{pH} + \text{pOH} = 14.00 \tag{14.2.16}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.903 = 12.10 \tag{14.2.17}$$

Exercise 14.2.3

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 14.2.5).



(a) (b)

Figure 14.2.5: (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; $\text{pH} = -\log \text{H}_3\text{O}^+$. The concentration of OH^- can be expressed as the pOH of the solution: $\text{pOH} = -\log[\text{OH}^-]$. In pure water, pH = 7.00 and pOH = 7.00

Key Equations

- $\text{pH} = -\log[\text{H}_3\text{O}^+]$
- $\text{pOH} = -\log[\text{OH}^-]$
- $[H_3O^+] = 10^{-\text{pH}}$
- $[OH^-] = 10^{-\text{pOH}}$
- pH + pOH = pK_w = 14.00 at 25 °C

Glossary

acidic
: describes a solution in which $[H_3O^+] > [OH^-]$

basic
: describes a solution in which $[H_3O^+] < [OH^-]$

neutral
: describes a solution in which $[H_3O^+] = [OH^-]$

pH
: logarithmic measure of the concentration of hydronium ions in a solution

pOH
: logarithmic measure of the concentration of hydroxide ions in a solution

Contributors and Attributions

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14.3: 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:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{14.3.1}$$

Water is the base that reacts with the acid HA, $\mathrm{A^-}$ is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ when the acid ionizes in water; Figure 14.3.1 lists several strong acids. A weak acid gives small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Figure 14.3.1: 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:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{14.3.2}$$

we write the equation for the ionization constant as:

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \tag{14.3.3}$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is also the solvent. If the solution is assumed to be dilute, the activity of the water is approximated by the activity of pure water, which is defined as having a value of 1. The larger the K_a of an acid, the larger the concentration of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ relative to the concentration of the nonionized acid, HA. Thus a stronger acid has a larger ionization constant than does a weaker acid. The ionization constants increase as the strengths of the acids increase.

The following data on acid-ionization constants indicate the order of acid strength: $\mathrm{CH_3CO_2H} < \mathrm{HNO_2} < \mathrm{HSO_4^-}$

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \qquad K_\mathrm{a} = 1.8 \times 10^{-5}$$

$$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{NO_2^-}(aq) \qquad K_\mathrm{a} = 4.6 \times 10^{-4}$$

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(aq) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq) \qquad K_\mathrm{a} = 1.2 \times 10^{-2}$$

Another measure of the strength of an acid is its *percent ionization*. The percent ionization of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\% \text{ ionization} = \frac{[H_3O^+]_{eq}}{[HA]_0} \times 100\% \tag{14.3.4}$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

Example 14.3.1: Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[H_3O^+]_{eq}}{[HNO_2]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq).$$

Since $10^{-pH} = [H_3O^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}\ M$, so that percent ionization (Equation 14.3.4) is:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

Exercise 14.3.1

Calculate the percent ionization of a 0.10 *M* solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq) \tag{14.3.5}$$

Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yields 100% (or very nearly so) of OH^- and HB^+ when it reacts with water; Figure 14.3.1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq), \tag{14.3.6}$$

we write the equation for the ionization constant as:

$$K_b = \frac{[HB^+][OH^-]}{[B]} \tag{14.3.7}$$

where the concentrations are those at equilibrium. Again, we do not include $[H_2O]$ in the equation because water is the solvent. The chemical reactions and ionization constants of the three bases shown are:

$$\mathrm{NO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HNO_2}(aq) + \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 2.17 \times 10^{-11}$$

$$\mathrm{CH_3CO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2H}(aq) + \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 5.6 \times 10^{-10}$$

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 1.8 \times 10^{-5}$$

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, $\mathrm{HA - A^-}$:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{14.3.8}$$

with $K_\mathrm{a} = \dfrac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$.

$$\mathrm{A^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OH^-}(aq) + \mathrm{HA}(aq) \tag{14.3.9}$$

with $K_\mathrm{b} = \dfrac{[\mathrm{HA}][\mathrm{OH}]}{[\mathrm{A^-}]}$.

Adding these two chemical equations yields the equation for the autoionization for water:

$$\cancel{\mathrm{HA}(aq)} + \mathrm{H_2O}(l) + \cancel{\mathrm{A^-}(aq)} + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \cancel{\mathrm{A^-}(aq)} + \mathrm{OH^-}(aq) + \cancel{\mathrm{HA}(aq)}$$

$$2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq)$$

As shown in the previous chapter on equilibrium, the K expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations' K expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that:

$$K_\mathrm{a} \times K_\mathrm{b} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \times \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = K_\mathrm{w} \tag{14.3.10}$$

For example, the acid ionization constant of acetic acid ($\mathrm{CH_3COOH}$) 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:

$$K_\mathrm{a} \times K_\mathrm{b} = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_\mathrm{w} \tag{14.3.11}$$

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base, $\mathrm{A^-}$, of the acid. If $\mathrm{A^-}$ is a strong base, any protons that are donated to water molecules are recaptured by $\mathrm{A^-}$. Thus there is relatively little $\mathrm{A^-}$ and $\mathrm{H_3O^+}$ in solution, and the acid, HA, is weak. If $\mathrm{A^-}$ is a weak base, water binds the protons more strongly, and the solution contains primarily $\mathrm{A^-}$ and $\mathrm{H_3O^+}$—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure 14.3.2).

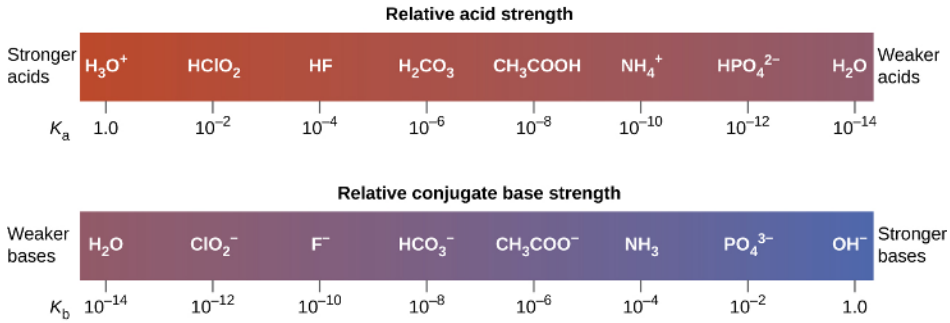


Figure 14.3.2: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure 14.3.3 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 14.3.3 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 14.3.3 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 14.3.3 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.

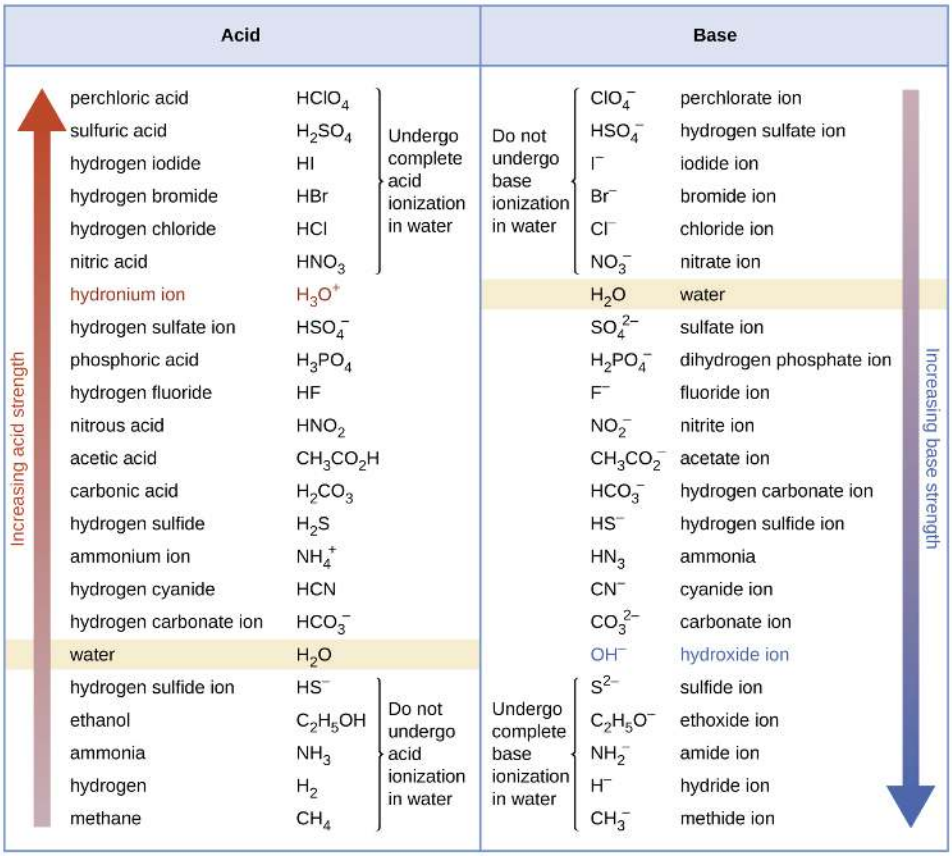


Figure 14.3.3: The chart shows the relative strengths of conjugate acid-base pairs.

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 14.3.3. 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 14.3.2: 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:

$$K_a = \frac{K_w}{K_b}$$
$$= \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}}$$
$$= 4.6 \times 10^{-4}$$

This answer can be verified by finding the K_a for HNO_2 in Table E1

? Exercise 14.3.2

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

- $K_a = \frac{[H_3O^+][A^-]}{[HA]}$
- $K_b = \frac{[HB^+][OH^-]}{[B]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w \text{ (at room temperature)}$

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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14.4: 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 (CH_3CO_2H) is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

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 14.4.1). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}$$



Figure 14.4.1: pH paper indicates that a 0.l-M solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[H_3O^+]$ = 0.1 M. A 0.1-M solution of CH_3CO_2H (beaker on right) has a pH of 3 ($[H_3O^+]$ = 0.001 M) because the weak acid CH_3CO_2H is only partially ionized. In this solution, $[H_3O^+] < [CH_3CO_2H]$. (credit: modification of work by Sahar Atwa)

Table 14.4.1: Ionization Constants of Some Weak Acids

Ionization Reaction	K_a at 25 °C
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	1.2×10^{-2}
$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	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}

Ionization Reaction	K_a at 25 °C
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9×10^{-10}

Table 14.4.1 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 14.4.2). 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:

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]}$$



Figure 14.4.2: 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 14.4.2 and Table E2.

Table 14.4.2: 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 14.4.3: 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:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)$$

$$\begin{aligned} K_\mathrm{a} &= \frac{[\mathrm{H_3O^+}][\mathrm{CH_3CO_2^-}]}{[\mathrm{CH_3CO_2H}]} \\ &= \frac{(0.00118)(0.00118)}{0.0787} \\ &= 1.77 \times 10^{-5} \end{aligned}$$

Exercise 14.4.3

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 14.4.4: 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 $[\mathrm{OH^-}] = 2.5 \times 10^{-3}\ M$?

Solution

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$\mathrm{C_8H_{10}N_4O_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{C_8H_{10}N_4O_2H^+}(aq) + \mathrm{OH^-}(aq)$$

so

$$K_\mathrm{b} = \frac{[\mathrm{C_8H_{10}N_4O_2H^+}][\mathrm{OH^-}]}{[\mathrm{C_8H_{10}N_4O_2}]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

Exercise 14.4.4

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 NaH_2PO_4 and Na_2HPO_4 at equilibrium with:

- $[OH^-] = 1.3 \times 10^{-6} M$
- $[H_2PO_4^-]$=0 · 042 M and
- $[HPO_4^{2-}]$=0 · 341 M.

Answer

K_b for $HPO_4^{2-} = 1.6 \times 10^{-7}$

Example 14.4.5: Determination of K_a or K_b from pH

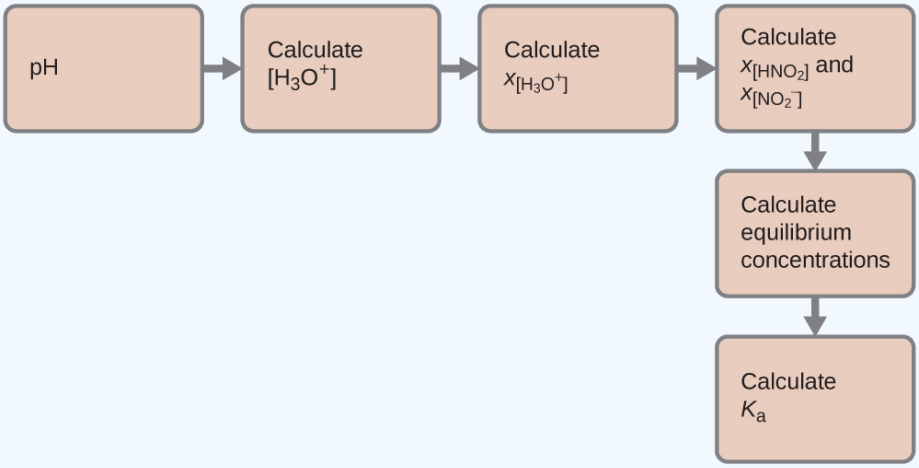
The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

Solution

We determine an equilibrium constant starting with the initial concentrations of HNO_2, H_3O^+, and NO_2^- as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the concentration of hydronium ion.)

We can solve this problem with the following steps in which *x* is a change in concentration of a species in the reaction:



We can summarize the various concentrations and changes as shown here (the concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its concentration):

	HNO_2 + H_2O ⇌	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* ~0 + *x*	$[NO_2]^-$ + *x* 0.0046

To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate $[H_3O^+]$, the equilibrium concentration of H_3O^+, from the pH:

$$[H_3O^+] = 10^{-2.34} = 0.0046\ M$$

The change in concentration of H_3O^+, $x_{[H_3O^+]}$, is the difference between the equilibrium concentration of H_3O^+, which we determined from the pH, and the initial concentration, $[H_3O^+]_i$. The initial concentration of H_3O^+ is its concentration in pure water, which is so much less than the final concentration that we approximate it as zero (~0).

The change in concentration of NO_2^- is equal to the change in concentration of $[H_3O^+]$. For each 1 mol of H_3O^+ that forms, 1 mol of NO_2^- forms. The equilibrium concentration of HNO_2 is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

	HNO_2 + H_2O ⇌	H_3O^+ +	NO_2^-
Initial concentration (*M*)	0.0516	~0	0
Change (*M*)	−*x*	+ *x* = 0.0046	*x* = 0.0046
Equilibrium concentration (*M*)	0.0470	0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

Exercise 14.4.5

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 14.4.6: Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid, HCO_2H, is the irritant that causes the body's reaction to ant stings.



The pain of an ant's sting is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH in a 0.534-*M* solution of formic acid?

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq) \quad K_a = 1.8 \times 10^{-4}$$

Solution

1. Determine x and equilibrium concentrations. The equilibrium expression is:

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq)$$

The concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its change in concentration when setting up the ICE table.

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

	HCO_2H +	H_2O ⇌	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:

$$K_a = 1.8 \times 10^{-4} = \frac{[H_3O^+][HCO_2^-]}{[HCO_2H]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

Now solve for x. Because the initial concentration of acid is reasonably large and K_a is very small, we assume that $x << 0.534$, which *permits* us to simplify the denominator term as $(0.534 - x) = 0.534$. This gives:

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

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:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534}$$

$$= 1.8 \times 10^{-2}\ (1.8\%\ \text{of}\ 0.534)$$

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:

$$[H_3O^+] = 0 + x = 0 + 9.8 \times 10^{-3}\ M.$$

$$= 9.8 \times 10^{-3}\ M$$

The pH of the solution can be found by taking the negative log of the $[H_3O^+]$, so:

$$pH = -\log(9.8 \times 10^{-3}) = 2.01$$

? Exercise 14.4.6: acetic acid

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \quad K_a = 1.8 \times 10^{-5}$$

Hint

Determine $[CH_3CO_2^-]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or $\frac{[CH_3CO_2^-]}{[CH_3CO_2H]_{\text{initial}}} \times 100$.

Answer

percent ionization = 1.3%

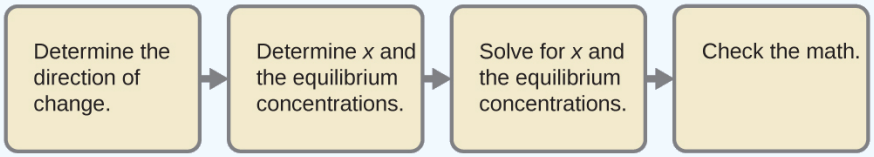
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

Example 14.4.7: Equilibrium Concentrations in a Solution of a Weak Base

Find the concentration of hydroxide ion in a 0.25-*M* solution of trimethylamine, a weak base:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq) \quad K_b = 6.3 \times 10^{-5}$$

Solution This problem requires that we calculate an equilibrium concentration by determining concentration changes as the ionization of a base goes to equilibrium. The solution is approached in the same way as that for the ionization of formic acid in Example 14.4.6. 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:

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{0.25 - x =} 6.3 \times 10^{-5}$$

If we assume that *x* is small relative to 0.25, then we can replace (0.25 − *x*) in the preceding equation with 0.25. Solving the simplified equation gives:

$$x = 4.0 \times 10^{-3}$$

This change is less than 5% of the initial concentration (0.25), so the assumption is justified.

Recall that, for this computation, x is equal to the equilibrium concentration of *hydroxide ion* in the solution (see earlier tabulation):

$$([OH^-] = 0 + x = x = 4.0 \times 10^{-3}\ M$$
$$= 4.0 \times 10^{-3}\ M$$

Then calculate pOH as follows:

$$pOH = -\log(4.3 \times 10^{-3}) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$pH + pOH = pK_w = 14.00$$

permits the computation of pH:

$$pH = 14.00 - pOH = 14.00 - 2.37 = 11.60$$

Check the work. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

Exercise 14.4.7

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 $\frac{[NH_4^+]}{[NH_3]} \times 100\%$

Answer a

$7.56 \times 10^{-4}\ M$, 2.33%

Answer b

2.33%

Some weak acids and weak bases ionize to such an extent that the simplifying assumption that x is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

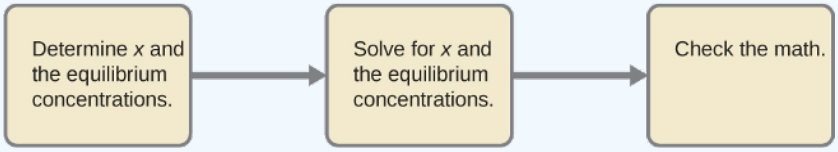
Example 14.4.8: Equilibrium Concentrations in a Solution of a Weak Acid

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	$\rightleftharpoons$	H_3O^+	+	SO_4^{2-}
Initial concentration (*M*)	0.50				~0		0
Change (*M*)	$-x$				x		x
Equilibrium concentration (*M*)	$0.50 + (-x) = 0.50 - x$				$0 + x = x$		$0 + x = x$

2. Solve for x and the concentrations.

As we begin solving for x, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of x.

At equilibrium:

$$K_a = 1.2 \times 10^{-2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(x)(x)}{0.50 - x}$$

If we assume that *x* is small and approximate (0.50 − *x*) as 0.50, we find:

$$x = 7.7 \times 10^{-2}$$

When we check the assumption, we confirm:

$$\frac{x}{[HSO_4^-]_i} \overset{?}{\leq} 0.05$$

which for this system is

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15(15\%)$$

The value of x is not less than 5% of 0.50, so the assumption is not valid. We need the quadratic formula to find x.

The equation:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

gives

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2} x = x^{2+}$$

or

$$x^{2+} + 1.2 \times 10^{-2} x - 6.0 \times 10^{-3} = 0$$

This equation can be solved using the quadratic formula. For an equation of the form

$$ax^{2+} + bx + c = 0,$$

x is given by the quadratic equation:

$$x = \frac{-b \pm \sqrt{b^{2+} - 4ac}}{2a}$$

In this problem, $a = 1$, $b = 1.2 \times 10^{-3}$, and $c = -6.0 \times 10^{-3}$.

Solving for x gives a negative root (which cannot be correct since concentration cannot be negative) and a positive root:

$$x = 7.2 \times 10^{-2}$$

Now determine the hydronium ion concentration and the pH:

$$\begin{aligned}[H_3O^+] &= 0 + x = 0 + 7.2 \times 10^{-2}\ M \\ &= 7.2 \times 10^{-2}\ M\end{aligned}$$

The pH of this solution is:

$$pH = -\log[H_3O^+] = -\log 7.2 \times 10^{-2} = 1.14$$

? Exercise 14.4.8

a. Show that the quadratic formula gives $x = 7.2 \times 10^{-2}$.
b. Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq) \quad K_b = 2.5 \times 10^{-4}$$

Hint

It will be necessary to convert $[OH^-]$ to $[H_3O^+]$ or pOH to pH toward the end of the calculation.

Answer

pH 11.16

The Relative Strengths of Strong Acids and Bases

Strong acids, such as HCl, HBr, and HI, all exhibit the same strength in water. The water molecule is such a strong base compared to the conjugate bases Cl^-, Br^-, and I^- that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find HCl, HBr, and HI differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol (a weaker base than water), the extent of ionization increases in the order $HCl < HBr < HI$, and so HI is demonstrated to be the strongest of these acids. The inability to discern differences in strength among strong acids dissolved in water is known as the leveling effect of water.

Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, O^{2-}, and the amide ion, NH_2^-, are such strong bases that they react completely with water:

$$O^{2-}(aq) + H_2O(l) \longrightarrow OH^-(aq) + OH^-(aq) \tag{14.4.1}$$

$$NH_2^-(aq) + H_2O(l) \longrightarrow NH_3(aq) + OH^-(aq) \tag{14.4.2}$$

Thus, O^{2-} and NH_2^- appear to have the same base strength in water; they both give a 100% yield of hydroxide ion.

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is $HF < HCl < HBr < HI$. Likewise, for group 16, the order of increasing acid strength is $H_2O < H_2S < H_2Se < H_2Te$. Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $CH_4 < NH_3 < H_2O < HF$; across the third row, it is $SiH_4 < PH_3 < H_2S < HCl$ (see Figure 14.4.3).

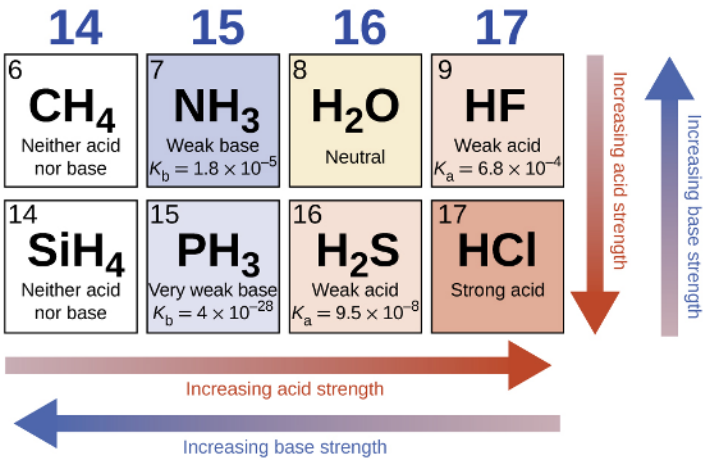
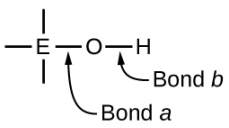


Figure 14.4.3: As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

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:



https://chem.libretexts.org/@go/page/531577

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 14.4.4).

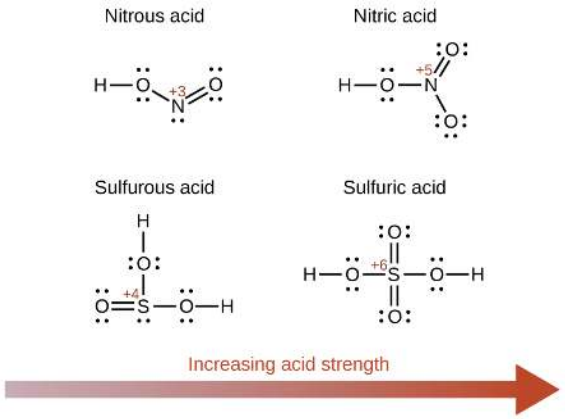


Figure 14.4.4: As the oxidation number of the central atom E increases, the acidity also increases.

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 $Al(H_2O)_3(OH)_3$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $Al(H_2O)_3(OH)_3$, is converted into the soluble ion, $[Al(H_2O)_2(OH)_4]^-$, by reaction with hydroxide ion:

$$[Al(H_2O)_3(OH)_3](aq) + OH^-(aq) \rightleftharpoons H_2O(l) + [Al(H_2O)_2(OH)_4]^-(aq)$$

In this reaction, a proton is transferred from one of the aluminum-bound H_2O molecules to a hydroxide ion in solution. The $Al(H_2O)_3(OH)_3$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion $[Al(H_2O)_6]^{3+}$ by reaction with hydronium ion:

$$3\,H_3O^+(aq) + Al(H_2O)_3(OH)_3(aq) \rightleftharpoons Al(H_2O)_6^{3+}(aq) + 3\,H_2O(l)$$

In this case, protons are transferred from hydronium ions in solution to $Al(H_2O)_3(OH)_3$, and the compound functions as a base.

Summary

The strengths of 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

- $K_\text{a} = \dfrac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$
- $K_\text{b} = \dfrac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w \text{ (at room temperature)}$
- $\text{Percent ionization} = \dfrac{[\text{H}_3\text{O}^+]_\text{eq}}{[\text{HA}]_0} \times 100$

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 H_3O^+, or any base stronger than OH^- will react with water to form H_3O^+, or OH^-, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

oxyacid

compound containing a nonmetal and one or more hydroxyl groups

percent ionization

ratio of the concentration of the ionized acid to the initial acid concentration, times 100

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14.5: 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 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:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq) \tag{14.5.1}$$

and the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3CO_2H]} \tag{14.5.2}$$

Sodium acetate (CH_3CO_2Na) is a strong electrolyte that ionizes completely in aqueous solution to produce Na^+ and $CH_3CO_2^-$ ions. If sodium acetate is added to a solution of acetic acid, Le Chatelier's principle predicts that the equilibrium in Equation 14.5.1 will shift to the left, consuming some of the added CH_3COO^- and some of the H^+ ions originally present in solution.

Because 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 $[H^+]$ is less than the initial value. Because $[H^+]$ 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, $[H^+]$ increases. Once again the equilibrium is temporarily disturbed, but the excess H^+ ions react with the conjugate base ($CH_3CO_2^-$), 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 $[CH_3CO_2^-]$ 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 $CH_3CO_2^-$, 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 14.5.1

A 0.150 M solution of formic acid at 25°C (pKa = 3.75) has a pH of 2.28 and is 3.5% ionized.

a. Is there a change to the pH of the solution if enough solid sodium formate is added to make the final formate concentration 0.100 M (assume that the formic acid concentration does not change)?
b. What percentage of the formic acid is ionized if 0.200 M HCl is added to the system?

Given: solution concentration and pH, pK_a, and percent ionization of acid; final concentration of conjugate base or strong acid added

Asked for: pH and percent ionization of formic acid

Strategy:

A. Write a balanced equilibrium equation for the ionization equilibrium of formic acid. Tabulate the initial concentrations, the changes, and the final concentrations.
B. Substitute the expressions for the final concentrations into the expression for Ka. Calculate $[H^+]$ and the pH of the solution.
C. Construct a table of concentrations for the dissociation of formic acid. To determine the percent ionization, determine the anion concentration, divide it by the initial concentration of formic acid, and multiply the result by 100.

Solution:

A Because sodium formate is a strong electrolyte, it ionizes completely in solution to give formate and sodium ions. The Na^+ ions are spectator ions, so they can be ignored in the equilibrium equation. Because water is both a much weaker acid than formic acid and a much weaker base than formate, the acid–base properties of the solution are determined solely by the formic acid ionization equilibrium:

$$HCO_2H(aq) \rightleftharpoons HCO_2^-(aq) + H^+(aq)$$

The initial concentrations, the changes in concentration that occur as equilibrium is reached, and the final concentrations can be tabulated.

Final Concentration

ICE	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
Initial	0.150	1.00×10^{-7}	0.100
Change	−x	+x	+x
Equilibrium	(0.150 − x)	x	(0.100 + x)

B We substitute the expressions for the final concentrations into the equilibrium constant expression and make our usual simplifying assumptions, so

$$\begin{aligned} K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} &= \frac{(x)(0.100+x)}{0.150-x} \\ &\approx \frac{x(0.100)}{0.150} \\ &\approx 10^{-3.75} \\ &\approx 1.8 \times 10^{-4} \end{aligned}$$

Rearranging and solving for x,

$$\begin{aligned} x &= (1.8 \times 10^{-4}) \times \frac{0.150\ M}{0.100\ M} \\ &= 2.7 \times 10^{-4} \\ &= [H^+] \end{aligned}$$

The value of x is small compared with 0.150 or 0.100 M, so our assumption about the extent of ionization is justified. Moreover,

$$K_a C_{HA} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5}$$

which is greater than 1.0×10^{-6}, so again, our assumption is justified. The final pH is:

$$pH = -\log(2.7 \times 10^{-4}) = 3.57$$

compared with the initial value of 2.29. Thus adding a salt containing the conjugate base of the acid has increased the pH of the solution, as we expect based on Le Chatelier's principle; the stress on the system has been relieved by the consumption of H^+ ions, driving the equilibrium to the left.

C Because HCl is a strong acid, it ionizes completely, and chloride is a spectator ion that can be neglected. Thus the only relevant acid–base equilibrium is again the dissociation of formic acid, and initially the concentration of formate is zero. We can construct a table of initial concentrations, changes in concentration, and final concentrations.

$$HCO_2H(aq) \leftrightharpoons H^+(aq) + HCO_2^-(aq)$$

initial concentrations, changes in concentration, and final concentrations

	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
initial	0.150	0.200	0
change	−x	+x	+x
final	(0.150 − x)	(0.200 + x)	x

To calculate the percentage of formic acid that is ionized under these conditions, we have to determine the final $[\mathrm{HCO_2^-}]$. 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,

$$\begin{aligned} x &= (1.80 \times 10^{-4}) \times \frac{0.150\ M}{0.200\ M} \\ &= 1.35 \times 10^{-4} = [HCO_2^-] \end{aligned}$$

Once again, our simplifying assumptions are justified. The percent ionization of formic acid is as follows:

$$\text{percent ionization} = \frac{1.35 \times 10^{-4}\ M}{0.150\ M} \times 100\% = 0.0900\%$$

Adding the strong acid to the solution, as shown in the table, decreased the percent ionization of formic acid by a factor of approximately 38 (3.45%/0.0900%). Again, this is consistent with Le Chatelier's principle: adding $\mathrm{H^+}$ ions drives the dissociation equilibrium to the left.

? Exercise 14.5.1

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%



A Video Discussing the Common Ion Effect: The Common Ion Effecr(opens in new window) [youtu.be]

The Common Ion Effect: Weak Bases Combined with Conjugate Acids

Now let's suppose we have a buffer solution that contains equimolar concentrations of a weak base (B) and its conjugate acid (BH^+). The general equation for the ionization of a weak base is as follows:

$$B(aq) + H_2O(l) \leftrightharpoons BH^+(aq) + OH^-(aq) \tag{14.5.3}$$

If the equilibrium constant for the reaction as written in Equation 14.5.3 is small, for example $K_b = 10^{-5}$, then the equilibrium constant for the reverse reaction is very large: $K = \dfrac{1}{K_b} = 10^5$. Adding a strong base such as OH^- to the solution therefore causes the equilibrium in Equation 14.5.3 to shift to the left, consuming the added OH^-. As a result, the OH^- ion concentration in solution remains relatively constant, and the pH of the solution changes very little. Le Chatelier's principle predicts the same outcome: when the system is stressed by an increase in the OH^- ion concentration, the reaction will proceed to the left to counteract the stress.

If the pK_b of the base is 5.0, the pK_a of its conjugate acid is

$$pK_a = pK_w - pK_b = 14.0 – 5.0 = 9.0.$$

Thus the equilibrium constant for ionization of the conjugate acid is even smaller than that for ionization of the base. The ionization reaction for the conjugate acid of a weak base is written as follows:

$$BH^+(aq) + H_2O(l) \leftrightharpoons B(aq) + H_3O^+(aq) \tag{14.5.4}$$

Again, the equilibrium constant for the reverse of this reaction is very large: K = $1/K_a$ = 10^9. If a strong acid is added, it is neutralized by reaction with the base as the reaction in Equation 14.5.4 shifts to the left. As a result, the H^+ ion concentration does not increase very much, and the pH changes only slightly. In effect, a buffer solution behaves somewhat like a sponge that can absorb H^+ and OH^- ions, thereby preventing large changes in pH when appreciable amounts of strong acid or base are added to a solution.

Buffers are characterized by the pH range over which they can maintain a more or less constant pH and by their buffer capacity, the amount of strong acid or base that can be absorbed before the pH changes significantly. Although the useful pH range of a buffer depends strongly on the chemical properties of the weak acid and weak base used to prepare the buffer (i.e., on K), its buffer capacity depends solely on the concentrations of the species in the buffered solution. The more concentrated the buffer solution, the greater its buffer capacity. As illustrated in Figure 14.5.1, 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.

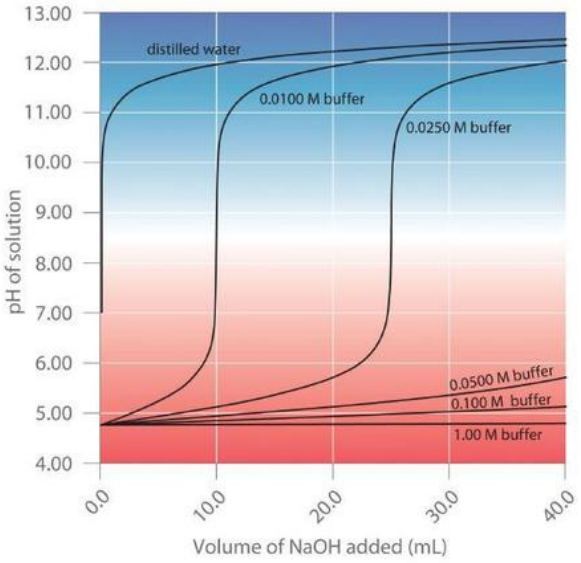


Figure 14.5.1: Effect of Buffer Concentration on the Capacity of a Buffer. (CC BY-SA-NC; Anonymous by request)
Graph of pH of solution against volume of NaOH added. Six different buffer concentrations are plotted.

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 $14.5.1$ 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:

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{14.5.5}$$

This equation can be rearranged as follows:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \tag{14.5.6}$$

Taking the logarithm of both sides and multiplying both sides by −1,

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right) \tag{14.5.7}$$

$$= -\log K_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{14.5.8}$$

Replacing the negative logarithms in Equation 14.5.8,

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{14.5.9}$$

or, more generally,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{14.5.10}$$

Equation 14.5.9 and Equation 14.5.10 are both forms of the Henderson-Hasselbalch approximation, named after the two early 20th-century chemists who first noticed that this rearranged version of the equilibrium constant expression provides an easy way to calculate the pH of a buffer solution. In general, the validity of the Henderson-Hasselbalch approximation may be limited to solutions whose concentrations are at least 100 times greater than their K_a values.

There are three special cases where the Henderson-Hasselbalch approximation is easily interpreted without the need for calculations:

- $[base] = [acid]$: Under these conditions,

  $$\frac{[base]}{[acid]} = 1$$

  in Equation 14.5.10. Because $\log 1 = 0$,

  $$pH = pK_a$$

  regardless of the actual concentrations of the acid and base. Recall that this corresponds to the midpoint in the titration of a weak acid or a weak base.
- $[base]/[acid] = 10$: In Equation 14.5.10, because $\log 10 = 1$,

  $$pH = pK_a + 1.$$
- $[base]/[acid] = 100$: In Equation 14.5.10, because $\log 100 = 2$,

  $$pH = pK_a + 2.$$

Each time we increase the [base]/[acid] ratio by 10, the pH of the solution increases by 1 pH unit. Conversely, if the [base]/[acid] ratio is 0.1, then pH = pK_a − 1. Each additional factor-of-10 decrease in the [base]/[acid] ratio causes the pH to decrease by 1 pH unit.

> If [base] = [acid] for a buffer, then pH = pK_a. Changing this ratio by a factor of 10 either way changes the pH by ±1 unit.

Example 14.5.2

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 14.5.9 or 14.5.10) to calculate the pH.

Solution:

According to the Henderson-Hasselbalch approximation (Equation 14.5.9), the pH of a solution that contains both a weak acid and its conjugate base is

$$pH = pK_a + \log([A-]/[HA]).$$

A

Inserting the given values into the equation,

$$pH = 3.75 + \log\left(\frac{0.215}{0.135}\right)$$
$$= 3.75 + \log 1.593$$
$$= 3.95$$

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,

$$pH = 3.75 + \log\left(\frac{0.0215}{0.0135}\right)$$
$$= 3.75 + \log 1.593$$
$$= 3.95$$

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 14.5.10, the more general form of the Henderson-Hasselbalch approximation, in which "base" and "acid" refer to the appropriate species of the conjugate acid–base pair. We are given [base] = [Py] = 0.119 M and $[acid] = [HPy^+] = 0.234\ M$. We also are given $pK_b = 8.77$ for pyridine, but we need pK_a for the pyridinium ion. Recall from Equation 16.23 that the pK_b of a weak base and the pK_a of its conjugate acid are related:

$$pK_a + pK_b = pK_w.$$

Thus pK_a for the pyridinium ion is $pK_w - pK_b = 14.00 - 8.77 = 5.23$. Substituting this pK_a value into the Henderson-Hasselbalch approximation,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$
$$= 5.23 + \log\left(\frac{0.119}{0.234}\right)$$
$$= 5.23\ -0.294$$
$$= 4.94$$

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 14.5.2

What is the pH of a solution that contains

a. 0.333 M benzoic acid and 0.252 M sodium benzoate?
b. 0.050 M trimethylamine and 0.066 M trimethylamine hydrochloride?

The pK_a of benzoic acid is 4.20, and the pK_b of trimethylamine is also 4.20.

Answer a

4.08

Answer b

9.68



A Video Discussing Using the Henderson Hasselbalch Equation: Using the Henderson Hasselbalch Equation(opens in new window) [youtu.be] (opens in new window)

The Henderson-Hasselbalch approximation ((Equation 14.5.9) can also be used to calculate the pH of a buffer solution after adding a given amount of strong acid or strong base, as demonstrated in Example 14.5.3

Example 14.5.3

The buffer solution in Example 14.5.2contained 0.135 M HCO_2H and 0.215 M 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 14.5.1. 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 14.5.10) to obtain the pH.

Solution:

The added HCl (a strong acid) or NaOH (a strong base) will react completely with formate (a weak base) or formic acid (a weak acid), respectively, to give formic acid or formate and water. We must therefore calculate the amounts of formic acid and formate present after the neutralization reaction.

A We begin by calculating the millimoles of formic acid and formate present in 100 mL of the initial pH 3.95 buffer:

$$100\ \cancel{mL}\left(\frac{0.135\,mmol\ HCO_2H}{\cancel{mL}}\right) = 13.5\,mmol\,HCO_2H$$

$$100\ \cancel{mL}\left(\frac{0.215\,mmol\ HCO_2^-}{\cancel{mL}}\right) = 21.5\,mmol\,HCO_2^-$$

The millimoles of H^+ in 5.00 mL of 1.00 M HCl is as follows:

$$5.00\ \cancel{mL}\left(\frac{1.00\,mmol\ H^+}{\cancel{mL}}\right) = 5\,mmol\,H^+$$

B Next, we construct a table of initial amounts, changes in amounts, and final amounts:

$$\mathrm{HCO^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_2H(aq)}$$

initial amounts, changes in amounts, and final amounts:

	$HCO^{2-}(aq)$	$H^+(aq)$	$HCO_2H(aq)$
Initial	21.5 mmol	5.00 mmol	13.5 mmol
Change	−5.00 mmol	−5.00 mmol	+5.00 mmol
Final	16.5 mmol	~0 mmol	18.5 mmol

The final amount of H^+ in solution is given as "~0 mmol." For the purposes of the stoichiometry calculation, this is essentially true, but remember that the point of the problem is to calculate the final $[H^+]$ and thus the pH. We now have all the information we need to calculate the pH. We can use either the lengthy procedure of Example 14.5.1 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 14.5.10):

$$\begin{aligned} pH &= pK_a + \log\left(\frac{[HCO_2^-]}{[HCO_2H]}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}/V_f}{n_{HCO_2H}/V_f}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \end{aligned}$$

Because the total volume appears in both the numerator and denominator, it cancels. We therefore need to use only the ratio of the number of millimoles of the conjugate base to the number of millimoles of the weak acid. So

$$\begin{aligned} pH &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \\ &= 3.75 + \log\left(\frac{16.5\ mmol}{18.5\ mmol}\right) \\ &= 3.75\ -0.050 = 3.70 \end{aligned}$$

Once again, this result makes sense on two levels. First, the addition of HClhas decreased the pH from 3.95, as expected. Second, the ratio of HCO_2^- to HCO_2H is slightly less than 1, so the pH should be between the pK_a and pK_a − 1.

A The procedure for solving this part of the problem is exactly the same as that used in part (a). We have already calculated the numbers of millimoles of formic acid and formate in 100 mL of the initial pH 3.95 buffer: 13.5 mmol of HCO_2H and 21.5 mmol of HCO_2^-. The number of millimoles of OH^- in 5.00 mL of 1.00 M $NaOH$ is as follows:

B With this information, we can construct a table of initial amounts, changes in amounts, and final amounts.

$$\mathrm{HCO_2H(aq) + OH^-(aq) \rightleftharpoons HCO_2^-(aq) + H_2O(l)}$$

initial amounts, changes in amounts, and final amounts

	$HCO_2H(aq)$	OH^-	$HCO_2^-(aq)$
Initial	13.5 mmol	5.00 mmol	21.5 mmol
Change	−5.00 mmol	−5.00 mmol	+5.00 mmol
Final	8.5 mmol	~0 mmol	26.5 mmol

The final amount of OH^- in solution is not actually zero; this is only approximately true based on the stoichiometric calculation. We can calculate the final pH by inserting the numbers of millimoles of both HCO_2^- and HCO_2H into the simplified Henderson-Hasselbalch expression used in part (a) because the volume cancels:

$$\begin{aligned} pH &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \\ &= 3.75 + \log\left(\frac{26.5\ mmol}{8.5\ mmol}\right) \\ &= 3.75 + 0.494 = 4.24 \end{aligned}$$

Once again, this result makes chemical sense: the pH has increased, as would be expected after adding a strong base, and the final pH is between the pK_a and pK_a + 1, as expected for a solution with a HCO_2^-/HCO_2H ratio between 1 and 10.

Exercise 14.5.3

The buffer solution from Example 14.5.2 contained 0.119 M pyridine and 0.234 M pyridine hydrochloride and had a pH of 4.94.

a. What is the final pH if 12.0 mL of 1.5 M NaOH are added to 250 mL of this solution?
b. What is the final pH if 12.0 mL of 1.5 M HCl are added?

Answer a

5.30

Answer b

4.42

Only the amounts (in moles or millimoles) of the acidic and basic components of the buffer are needed to use the Henderson-Hasselbalch approximation, not their concentrations.



A Video Discussing the Change in pH with the Addition of a Strong Acid to a Buffer: The Change in pH with the Addition of a Strong Acid to a Buffer(opens in new window) [youtu.be]



The Change in pH with the Addition of a Strong Base to a Buffer:

The Change in pH with the Addition of a Strong Base to a Buffer (opens in new window) [youtu.be]

The results obtained in Example 14.5.3 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 14.5.2 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.

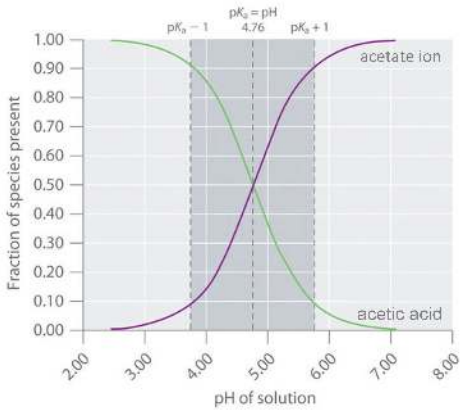


Figure 14.5.2: Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid. The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable concentrations of both species are present (pH 3.76–5.76, corresponding to $pH = pK_a \pm 1$). (CC BY-SA-NC; Anonymous by request)

Graph of mole fraction against pH of solution. The green line is acetic acid and the purple line is the acetate ion.



A Video Discussing The Buffer Region: The Buffer Region (opens in new window) [youtu.be]

The Relationship between Titrations and Buffers

There is a strong correlation between the effectiveness of a buffer solution and the titration curves discussed in Section 16.5. Consider the schematic titration curve of a weak acid with a strong base shown in Figure 14.5.3. 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.

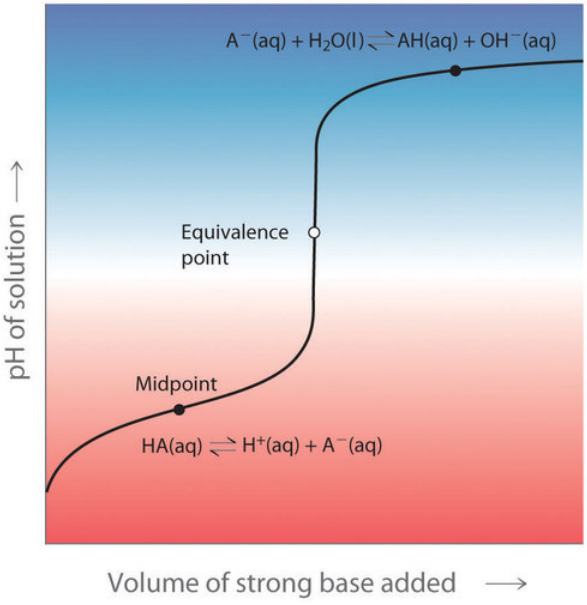


Figure 14.5.3: The Relationship between Titration Curves and Buffers. (CC BY-SA-NC; Anonymous by request)

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:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \tag{14.5.11}$$

with $K_a = 4.5 \times 10^{-7}$ and $pK_a = 6.35$ at 25°C. In fact, Equation 14.5.11 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 14.5.11does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C.

As shown in Equation 14.5.12, 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:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \tag{14.5.12}$$

with $K' = 4.0 \times 10^{-3}$ at 37°C. The true pK_a of carbonic acid at 37°C is therefore 3.70, not 6.35, corresponding to a K_a of 2.0×10^{-4}, which makes it a much stronger acid than Equation 14.5.11 suggests. Adding Equation 14.5.11 and Equation 14.5.12and 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:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \tag{14.5.13}$$

with $K' = 4.0 \times 10^{-3} (37^\circ C)$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \tag{14.5.14}$$

with $K_a = 2.0 \times 10^{-4} (37^\circ C)$

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \tag{14.5.15}$$

with $K = 8.0 \times 10^{-7} (37^\circ C)$

The K value for the reaction in Equation 14.5.15is 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

$$K = \frac{[H^+][HCO_3^-]}{[CO_2]} = 8.0 \times 10^{-7} \tag{14.5.16}$$

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 14.5.16,

$$K = \frac{[H^+][HCO_3^-]}{(3.0 \times 10^{-5}\ M/mmHg)(P_{CO_2})}$$

where P_{CO_2} is in mmHg. Taking the negative logarithm of both sides and rearranging,

$$pH = 6.10 + \log\left(\frac{[HCO_3^-]}{(3.0 \times 10^{-5} M/mm\ Hg)\ (P_{CO_2})}\right) \tag{14.5.17}$$

Thus the pH of the solution depends on both the CO_2 pressure over the solution and $[HCO_3^-]$. Figure 14.5.4 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.

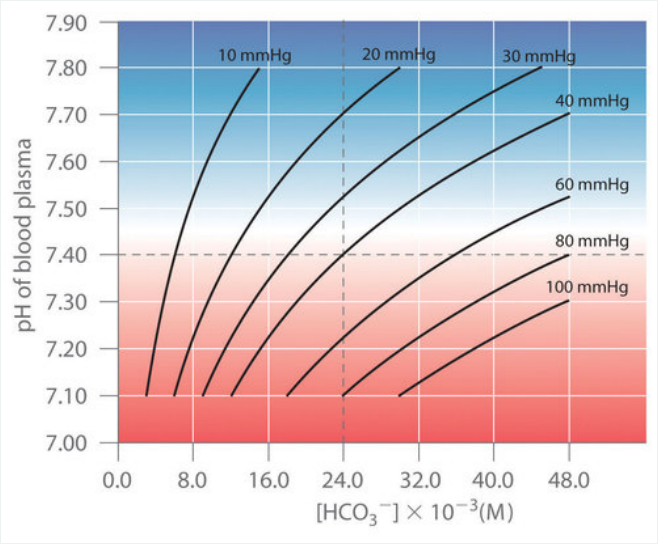


Figure 14.5.4: Buffering in Blood: pH versus $[HCO_3^-]$ Curves for Buffers with Different Values of P_{CO_2}. Only those combinations of pH and $[HCO_3^-]$ that lie on a given line are allowed for the particular value of P_{CO_2} indicated. Normal values of blood plasma pH and $[HCO_3^-]$ are indicated by dashed lines. (CC BY-SA-NC; Anonymous by request)

According to Equation 14.5.17, adding a strong acid to the CO_2/HCO_3^- system causes $[HCO_3^-]$ to decrease as HCO_3^- is converted to CO_2. Excess CO_2 is released in the lungs and exhaled into the atmosphere, however, so there is essentially no change in P_{CO_2}. Because the change in $[HCO_3^-]/P_{CO_2}$ is small, Equation 14.5.17 predicts that the change in pH will also be rather small. Conversely, if a strong base is added, the OH^- reacts with CO_2 to form HCO_3^-, but CO_2 is replenished by the body, again limiting the change in both $[HCO_3^-]/P_{CO_2}$ and pH. The 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_{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 $[HCO_3^-]$. The increase in pH and decrease in $[HCO_3^-]$ in response to the decrease in P_{CO_2} are responsible for the general malaise that many people experience at high altitudes. If their blood pH does not adjust rapidly, the condition can develop into the life-threatening phenomenon known as altitude sickness.



A Video Summary of the pH Curve for a Strong Acid/Strong Base Titration:

Summary of the pH Curve for a Strong Acid/Strong Base Titration(opens in new window) [youtu.be]

Summary

Buffers are solutions that resist a change in pH after adding an acid or a base. Buffers contain a weak acid (HA) and its conjugate weak base (A^-). Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium shifts the equilibrium in such a way as to reduce the concentration of the common ion. The shift in equilibrium is called the common ion effect. Buffers are characterized by their pH range and buffer capacity. The useful pH range of a buffer depends strongly on the chemical properties of the conjugate weak acid–base pair used to prepare the buffer (the K_a or K_b), whereas its buffer capacity depends solely on the concentrations of the species in the solution. The pH of a buffer can be calculated using the Henderson-Hasselbalch approximation, which is valid for solutions whose concentrations are at least 100 times greater than their K_a values. Because no single buffer system can effectively maintain a constant pH value over the physiological range of approximately 5 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

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14.6: 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 14.6.1*a* 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 14.6.1*b* 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.

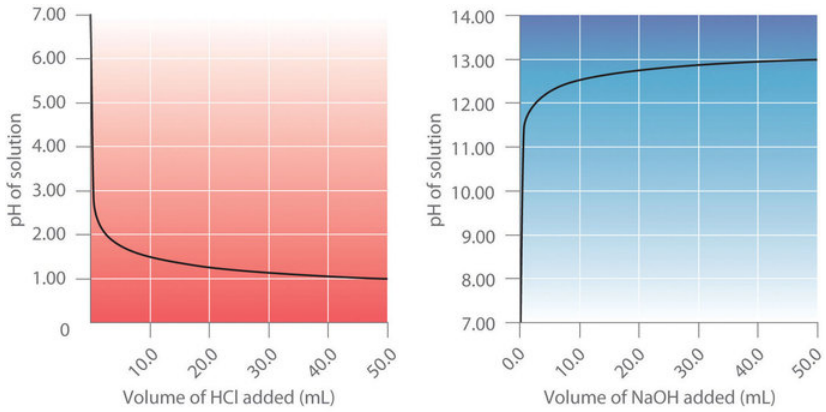


Figure 14.6.1: Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water. (a) When 0.20 M HCl is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 M HCl. (b) Conversely, when 0.20 M NaOH is added to 50.0 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 14.6.2*a*):

$$OH^- + H^+ \rightleftharpoons H_2O.$$

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:

$$moles\ of\ base = (volume)_b(molarity)_b V_b M_b = moles\ of\ acid = (volume)_a(molarity)_a = V_a M_a \qquad (14.6.1)$$

If 0.20 M NaOH is added to 50.0 mL of a 0.10 M solution of HCl, we solve for V_b:

$$V_b(0.20Me) = 0.025L = 25mL$$

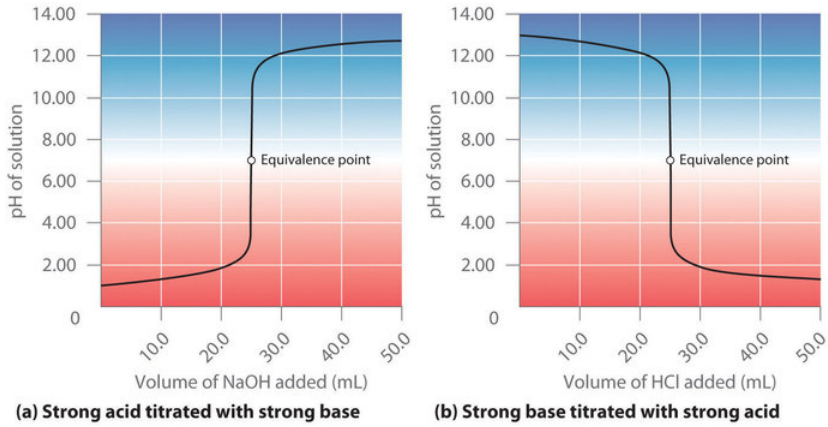


Figure 14.6.2: The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid(a) As 0.20 M NaOH is slowly added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases slowly 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 $14.6.2b$, 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 $14.6.2a$. 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 14.6.1: Hydrochloric Acid

Calculate the pH of the solution after 24.90 mL of 0.200 M NaOH has been added to 50.00 mL of 0.100 M HCl.

Given: volumes and concentrations of strong base and acid

Asked for: pH

Strategy:

A. Calculate the number of millimoles of H^+ and OH^- to determine which, if either, is in excess after the neutralization reaction has occurred. If one species is in excess, calculate the amount that remains after the neutralization reaction.
B. Determine the final volume of the solution. Calculate the concentration of the species in excess and convert this value to pH.

Solution

A Because 0.100 mol/L is equivalent to 0.100 mmol/mL, the number of millimoles of H^+ in 50.00 mL of 0.100 M HCl can be calculated as follows:

$$50.00\ \cancel{mL}\left(\frac{0.100\ mmol\ HCl}{\cancel{mL}}\right) = 5.00\ mmol\ HCl = 5.00\ mmol\ H^+$$

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 H^+ is in excess. To completely neutralize the acid requires the addition of 5.00 mmol of OH^- to the HCl solution. Because only 4.98 mmol of OH^- has been added, the amount of excess 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 H^+ is as follows:

$$[H^+] = \frac{0.02\ mmol\ H^+}{74.90\ mL} = 3 \times 10^{-4}\ M$$

Hence,

$$pH \approx -\log[H^+] = -\log(3 \times 10^{-4}) = 3.5$$

This is significantly less than the pH of 7.00 for a neutral solution.

Exercise 14.6.1

Calculate the pH of a solution prepared by adding $40.00\ mL$ of $0.237\ M\ HCl$ to $75.00\ mL$ of a $0.133 M$ solution of $NaOH$.

Answer

11.6



pH after the addition of 10 ml of Strong Base to a Strong Acid:

https://youtu.be/_cM1_-kdJ20 (opens in new window)



pH at the Equivalence Point in a Strong Acid/Strong Base Titration:

https://youtu.be/7POGDA5Ql2M

Titrations of Weak Acids and Bases

In contrast to strong acids and bases, the shape of the titration curve for a weak acid or a weak base depends dramatically on the identity of the acid or the base and the corresponding K_a or K_b. As we shall see, the pH also changes much more gradually around the equivalence point in the titration of a weak acid or a weak base. As you learned previously, $[\mathrm{H}^+]$ of a solution of a weak acid (HA) is not equal to the concentration of the acid but depends on both its pK_a and its concentration. Because only a fraction of a weak acid dissociates, $[\backslash(\mathrm{H}^+]$ is less than $[\mathrm{HA}]$. Thus the pH of a solution of a weak acid is greater than the pH of a solution of a strong acid of the same concentration.

Figure $14.6.3a$ 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 $14.6.2$ 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.

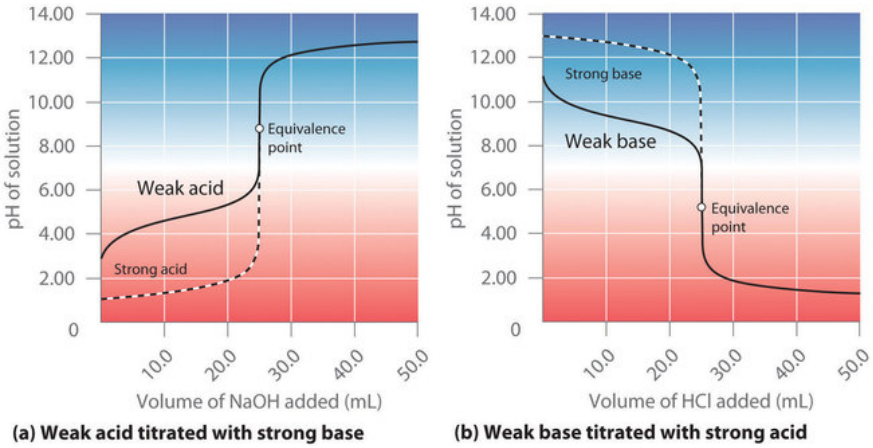


Figure 14.6.3: The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid. (a) As 0.200 M NaOH is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more 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 $14.6.3a$ 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 $14.6.2$ 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:

$$pH = -\log(1.32 \times 10^{-3}) = 2.879$$



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 14.6.3). Because the neutralization reaction proceeds to completion, all of the OH^- ions added will react with the acetic acid to generate acetate ion and water:

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightarrow CH_3CO^-_{2\ (aq)} + H_2O_{(l)} \tag{14.6.2}$$

All problems of this type must be solved in two steps: a stoichiometric calculation followed by an equilibrium calculation. In the first step, we use the stoichiometry of the neutralization reaction to calculate the amounts of acid and conjugate base present in solution after the neutralization reaction has occurred. In the second step, we use the equilibrium equation to determine $[H^+]$ 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.

$$\mathrm{CH_3CO_2H(aq) + OH^-(aq) \rightleftharpoons CH_3CO_2^-(aq) + H_2O(l)}$$

ICE table

ICE	$[\mathrm{CH_3CO_2H}]$	$[\mathrm{OH^-}]$	$[\mathrm{CH_3CO_2^-}]$
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 $[\mathrm{H^+}]$ at equilibrium following the addition of $NaOH$, we must first calculate $[\mathrm{CH_3CO_2H}]$ and $[\mathrm{CH_3CO_2^-}]$ using the number of millimoles of each and the total volume of the solution at this point in the titration:

$$final\ volume = 50.00\ mL + 5.00\ mL = 55.00\ mL$$

$$[CH_3CO_2H] = \frac{4.00\ mmol\ CH_3CO_2H}{55.00\ mL} = 7.27 \times 10^{-2}\ M$$

$$\left[CH_3CO_2^-\right] = \frac{1.00\ mmol\ CH_3CO_2^-}{55.00\ mL} = 1.82 \times 10^{-2}\ M$$

Knowing the concentrations of acetic acid and acetate ion at equilibrium and K_a for acetic acid (1.74×10^{-5}), we can calculate $[H^+]$ at equilibrium:

$$K_a = \frac{\left[CH_3CO_2^-\right][H^+]}{[CH_3CO_2H]}$$

$$\left[H^+\right] = \frac{K_a\,[CH_3CO_2H]}{\left[CH_3CO_2^-\right]} = \frac{\left(1.72 \times 10^{-5}\right)\left(7.27 \times 10^{-2}\ M\right)}{\left(1.82 \times 10^{-2}\right)} = 6.95 \times 10^{-5}\ M$$

Calculating $-\log[\mathrm{H^+}]$ gives

$$pH = -\log(6.95 \times 10^{-5}) = 4.158.$$

Comparing the titration curves for HCl and acetic acid in Figure 14.6.3*a*, 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 14.6.2, we calculate another point for constructing the titration curve of acetic acid.



pH Before the Equivalence Point of a Weak Acid/Strong Base Titration:

https://youtu.be/znpwGCsefXc

Example 14.6.2

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 $K_w = K_a K_b$. Calculate [OH−] and use this to calculate the pH of the solution.

Solution

A Ignoring the spectator ion (Na^+), the equation for this reaction is as follows:

$$CH_3CO_2H_{(aq)} + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l)$$

The initial numbers of millimoles of OH^- and CH_3CO_2H are as follows:

$$25.00 \text{ mL}(0.200 \text{ mmol OH}-\text{mL}=5.00 \text{ mmol } OH-$$

$$50.00\ mL(0.100 CH_3CO_2HL = 5.00 mmol\ CH_3CO_2H$$

The number of millimoles of OH^- equals the number of millimoles of CH_3CO_2H, so neither species is present in excess.

B Because the number of millimoles of OH^- added corresponds to the number of millimoles of acetic acid in solution, this is the equivalence point. The results of the neutralization reaction can be summarized in tabular form.

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3CO_2^-(aq) + H_2O(l)$$

results of the neutralization reaction

ICE	$[CH_3CO_2H]$	$[OH^-]$	$[CH_3CO_2^-]$
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:

$$[\mathrm{CH_3CO_2}] = \frac{5.00\ mmol\ CH_3CO_2^-}{(50.00+25.00)\ mL} = 6.67\times10^{-2}\ M$$

The equilibrium reaction of acetate with water is as follows:

$$\mathrm{CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)}$$

The equilibrium constant for this reaction is

$$K_b = \frac{K_w}{K_a} \tag{14.6.3}$$

where K_a is the acid ionization constant of acetic acid. We therefore define x as $[\mathrm{OH^-}]$ produced by the reaction of acetate with water. Here is the completed table of concentrations:

$$H_2O_{(l)} + CH_3CO_{2(aq)}^- \rightleftharpoons CH_3CO_2H_{(aq)} + OH_{(aq)}^-$$

completed table of concentrations

	$[\mathrm{CH_3CO_2^-}]$	$[\mathrm{CH_3CO_2H}]$	$[\mathrm{OH^-}]$
initial	0.0667	0	1.00 × 10−7
change	−x	+x	+x
final	(0.0667 − x)	x	x

D We can obtain K_b by substituting the known values into Equation 14.6.3:

$$K_b = \frac{K_w}{K_a} = \frac{1.01\times10^{-14}}{1.74\times10^{-5}} = 5.80\times10^{-10} \tag{14.6.4}$$

Substituting the expressions for the final values from the ICE table into Equation 14.6.4 and solving for x:

$$\frac{x^2}{0.0667} = 5.80\times10^{-10}$$

$$x = \sqrt{(5.80\times10^{-10})(0.0667)}$$

$$= 6.22\times10^{-6}$$

Thus $[OH^-] = 6.22\times10^{-6}\ M$ and the pH of the final solution is 8.794 (Figure 14.6.3*a*). 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 14.6.2

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 14.6.3, 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 $14.6.4$ 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.

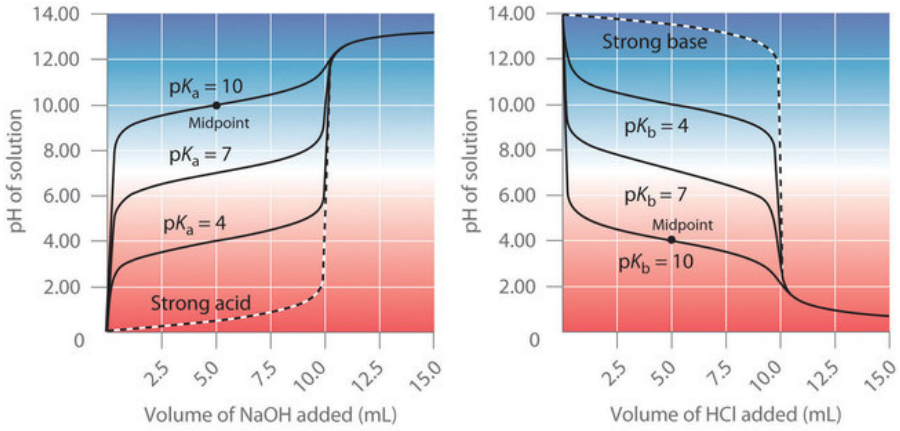


Figure 14.6.4: Effect of Acid or Base Strength on the Shape of Titration Curves. Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the pK_a or pK_b of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M NaOH added 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 $14.6.4a$ and $14.6.4b$ for the two shallowest curves. By definition, at the midpoint of the titration of an acid, [HA] = [A−]. Recall that the ionization constant for a weak acid is as follows:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

If $[HA] = [A^-]$, this reduces to $K_a = [H_3O^+]$. Taking the negative logarithm of both sides,

$$-\log K_a = -\log[H_3O+]$$

From the definitions of pK_a and pH, we see that this is identical to

$$pK_a = pH \tag{14.6.5}$$

Thus the pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid, as indicated in part (a) in Figure $14.6.4$ 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 $14.6.5$ 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.

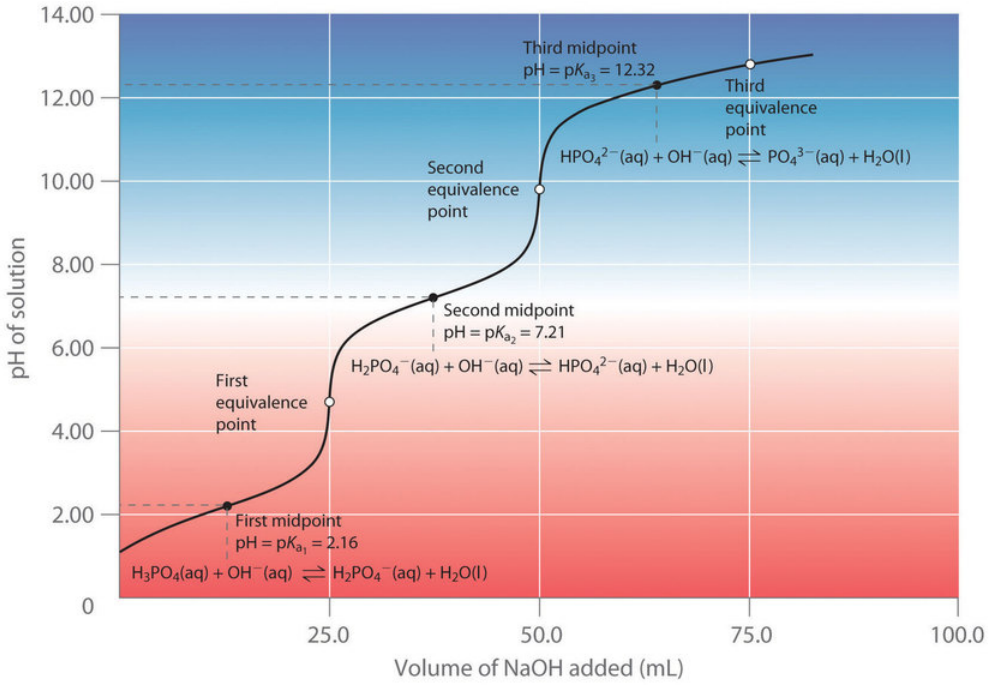
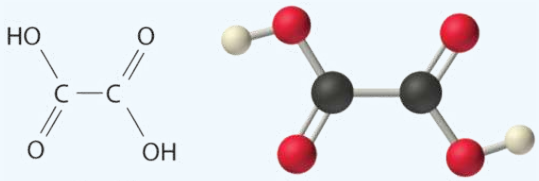


Figure 14.6.5: Titration Curve for Phosphoric Acid (H_3PO_4, a Typical Polyprotic Acid. The curve for the titration of 25.0 mL of a 0.100 M H_3PO_4 solution with 0.100 M NaOH along with the species in solution at each Ka is shown. Note the two distinct equivalence points corresponding to deprotonation 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 14.6.5. 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 14.6.3

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 (HO_2CCO_2H), a diprotic acid (abbreviated as 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 ($O_2CCO_2^{2-}$, 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 14.6.2:

$$\text{final volume of solution} = 100.0\,mL + 55.0\,mL = 155.0\,mL$$

Thus the concentrations of Hox^- and ox^{2-} are as follows:

$$\left[Hox^-\right] = \frac{3.60\ mmol\ Hox^-}{155.0\ mL} = 2.32 \times 10^{-2}\ M$$

$$\left[ox^{2-}\right] = \frac{1.50\ mmol\ ox^{2-}}{155.0\ mL} = 9.68 \times 10^{-3}\ M$$

We can now calculate [H+] at equilibrium using the following equation:

$$K_{a2} = \frac{\left[ox^{2-}\right]\left[H^+\right]}{\left[Hox^-\right]}$$

Rearranging this equation and substituting the values for the concentrations of Hox^- and ox^{2-},

$$\left[H^+\right] = \frac{K_{a2}\left[Hox^-\right]}{\left[ox^{2-}\right]} = \frac{\left(1.6 \times 10^{-4}\right)\left(2.32 \times 10^{-2}\right)}{\left(9.68 \times 10^{-3}\right)} = 3.7 \times 10^{-4}\ M$$

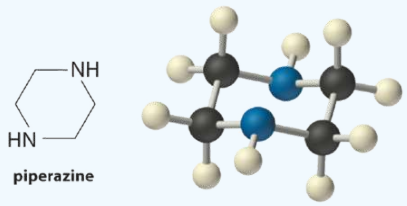
So

$$pH = -\log\left[H^+\right] = -\log\left(3.7 \times 10^{-4}\right) = 3.43$$

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 14.6.3: Piperazine

Piperazine is a diprotic base used to control intestinal parasites ("worms") in pets and humans. A dog is given 500 mg (5.80 mmol) of piperazine (pK_{b1} = 4.27, pK_{b2} = 8.67). If the dog's stomach initially contains 100 mL of 0.10 M HCl (pH = 1.00), calculate the pH of the stomach contents after ingestion of the piperazine.



Answer

pH=4.9

Indicators

In practice, most acid–base titrations are not monitored by recording the pH as a function of the amount of the strong acid or base solution used as the titrant. Instead, an acid–base indicator is often used that, if carefully selected, undergoes a dramatic color change at the pH corresponding to the equivalence point of the titration. Indicators are weak acids or bases that exhibit intense colors that vary with pH. The conjugate acid and conjugate base of a good indicator have very different colors so that they can be distinguished easily. Some indicators are colorless in the conjugate acid form but intensely colored when deprotonated (phenolphthalein, for example), which makes them particularly useful.

We can describe the chemistry of indicators by the following general equation:

$$\mathrm{HIn(aq)} \rightleftharpoons \mathrm{H^+(aq) + In^-(aq)}$$

where the protonated form is designated by HIn and the conjugate base by $\mathrm{In^-}$. The ionization constant for the deprotonation of indicator HIn is as follows:

$$K_{In} = \frac{[\mathrm{H^+}][\mathrm{In^-}]}{[\mathrm{HIn}]} \tag{14.6.6}$$

The pK_{in} (its pK_a) determines the pH at which the indicator changes color.

Many different substances can be used as indicators, depending on the particular reaction to be monitored. For example, red cabbage juice contains a mixture of colored substances that change from deep red at low pH to light blue at intermediate pH to yellow at high pH. Similarly, *Hydrangea macrophylla* flowers can be blue, red, pink, light purple, or dark purple depending on the soil pH (Figure 14.6.6). 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 14.6.6: 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 14.6.7 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

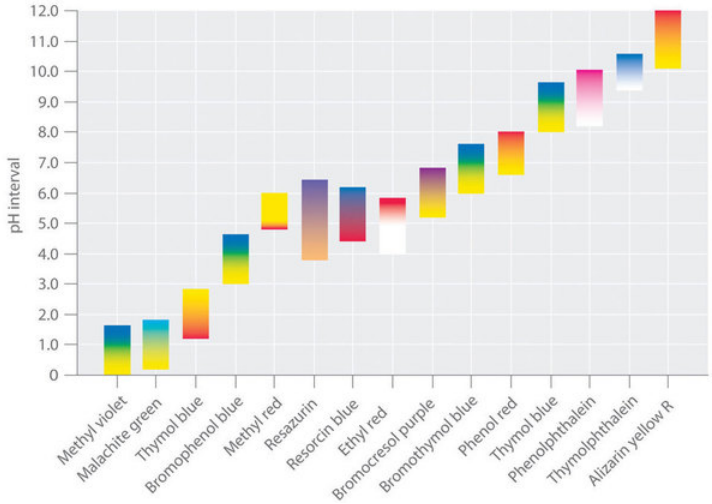


Figure 14.6.7: Some Common Acid–Base Indicators. Approximate colors are shown, along with pK_{in} values and the pH range over which the color changes. (CC BY-SA-NC; Anonymous by request)

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 14.6.8 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.

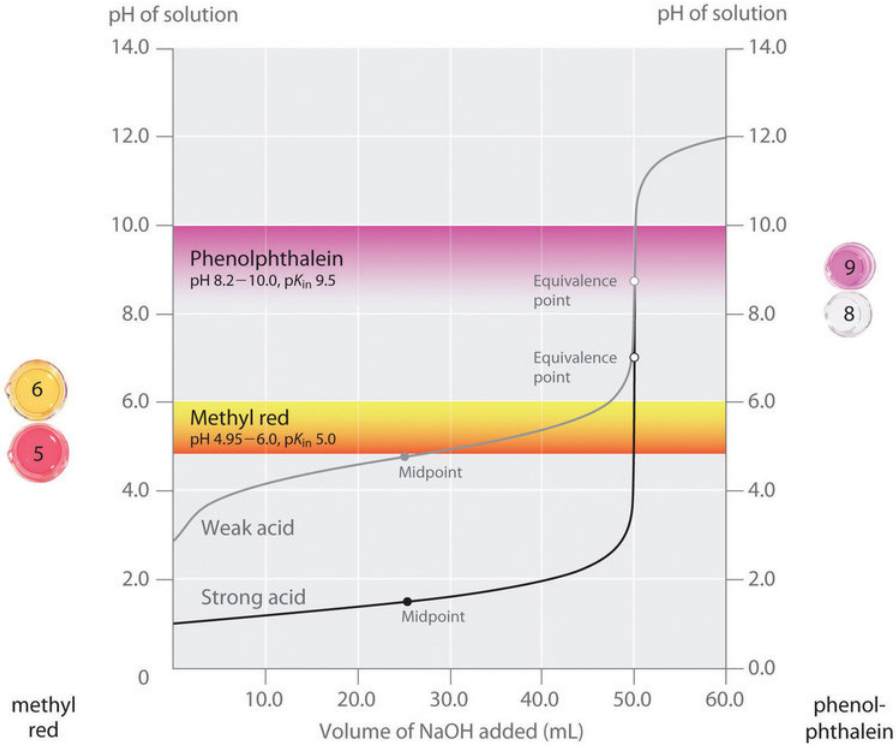


Figure 14.6.8: Choosing the Correct Indicator for an Acid–Base Titration. (CC BY-SA-NC; Anonymous by request)

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 14.6.9).

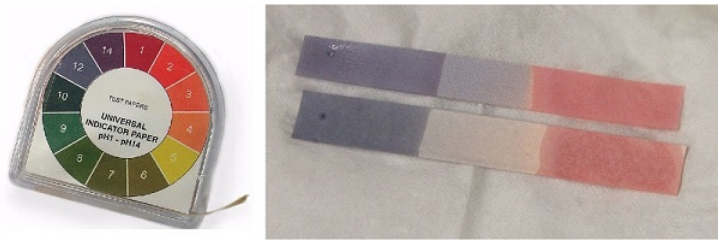


Figure 14.6.9: pH Paper. pH paper contains a set of indicators that change color at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the color to the standards provided. (CC BY-SA-NC; Anonymous by request)



pH Indicators: pH Indicators(opens in new window) [youtu.be]

Summary and Takeaway

Plots of acid–base titrations generate titration curves that can be used to calculate the pH, the pOH, the pK_a, and the pK_b of the system. The shape of a titration curve, a plot of pH versus the amount of acid or base added, provides important information about what is occurring in solution during a titration. The shapes of titration curves for weak acids and bases depend dramatically on the identity of the compound. The equivalence point of an acid–base titration is the point at which exactly enough acid or base has been added to react completely with the other component. The equivalence point in the titration of a strong acid or a strong base occurs at pH 7.0. In titrations of weak acids or weak bases, however, the pH at the equivalence point is greater or less than 7.0, respectively. The pH tends to change more slowly before the equivalence point is reached in titrations of weak acids and weak bases than in titrations of strong acids and strong bases. The pH at the midpoint, the point halfway on the titration curve to the equivalence point, is equal to the pK_a of the weak acid or the pK_b of the weak base. Thus titration methods can be used to determine both the concentration and the pK_a (or the pK_b) of a weak acid (or a weak base). Acid–base indicators are compounds that change color at a particular pH. They are typically weak acids or bases whose changes in color correspond to deprotonation or protonation of the indicator itself.

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14.7: Polyprotic Acids

Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

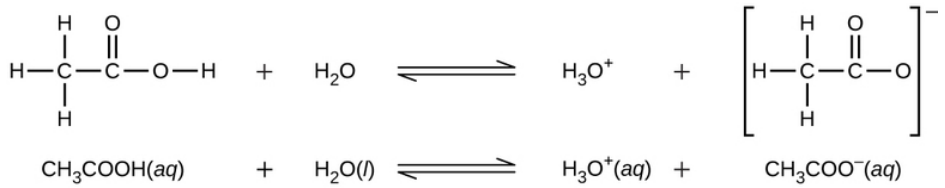
We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, HNO_3, and HCN that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

$$HCN(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CN^-(aq)$$

Even though it contains four hydrogen atoms, acetic acid, CH_3CO_2H, is also monoprotic because only the hydrogen atom from the carboxyl group ($-COOH$) reacts with bases:



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**

$$H_2SO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_4^-(aq)$$

with $K_{a1} > 10^2$; *complete dissociation*.

- **The second ionization is**

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

with $K_{a2} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids. When we make a solution of a weak diprotic acid, we get a solution that contains a mixture of acids. Carbonic acid, H_2CO_3, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

- **First Ionization**

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

with

$$K_{\mathrm{H_2CO_3}} = \frac{[\mathrm{H_3O^+}][\mathrm{HCO_3^-}]}{[\mathrm{H_2CO_3}]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

- **Second Ionization**

$$\mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CO_3^{2-}}(aq)$$

with

$$K_{\mathrm{HCO_3^-}} = \frac{[\mathrm{H_3O^+}][\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]} = 4.7 \times 10^{-11}$$

$K_{\mathrm{H_2CO_3}}$ is larger than $K_{\mathrm{HCO_3^-}}$ by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that little of the $\mathrm{HCO_3^-}$ formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and $\mathrm{HCO_3^-}$ are practically equal in a pure aqueous solution of H_2CO_3.

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This can simplify our work considerably because we can determine the concentration of H_3O^+ and the conjugate base from the first ionization, then determine the concentration of the conjugate base of the second ionization in a solution with concentrations determined by the first ionization.

Example 14.7.1: Ionization of a Diprotic Acid

When we buy soda water (carbonated water), we are buying a solution of carbon dioxide in water. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are $[\mathrm{H_3O^+}]$, $[\mathrm{HCO_3^-}]$, and $[\mathrm{CO_3^{2-}}]$ in a saturated solution of CO_2 with an initial $[H_2CO_3]$ = 0.033 *M*?

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \quad K_{\mathrm{a1}} = 4.3 \times 10^{-7} \qquad \text{(equilibrium step 1)}$$

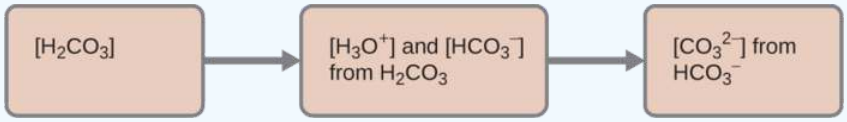
$$\mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CO_3^{2-}}(aq) \quad K_{\mathrm{a2}} = 4.7 \times 10^{-11} \qquad \text{(equilibrium step 2)}$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than $\mathrm{HCO_3^-}$, so $\mathrm{H_2CO_3}$ is the dominant producer of hydronium ion in solution. Thus there are two parts in the solution of this problem:

1. Using the customary four steps, we determine the concentration of H_3O^+ and $\mathrm{HCO_3^-}$ produced by ionization of H_2CO_3.
2. Then we determine the concentration of $\mathrm{CO_3^{2-}}$ in a solution with the concentration of H_3O^+ and $\mathrm{HCO_3^-}$ determined in (1).

To summarize:



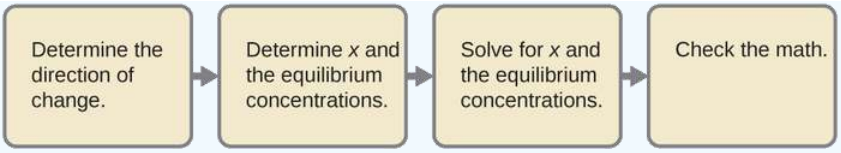
Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “left bracket H subscript 2 C O subscript 3 right bracket.” The second is labeled “left bracket H subscript 3 O superscript plus right bracket and left bracket H C O subscript 3 superscript negative right bracket from H subscript 2 C O subscript 3.” The third is labeled “left bracket C O subscript 3 superscript 2 negative right bracket from H C O subscript 3 superscript negative.”

1. First Ionization: Determine the concentrations of $\mathrm{H_3O^+}$ *and* $\mathrm{HCO_3^-}$.

Since equilibrium step 1 is has a much bigger $K_{a1} = 4.3 \times 10^{-7}$ than $K_{a2} = 4.7 \times 10^{-11}$ for equilibrium step 2, we can safely ignore the second ionization step and focus only on the first step (but address it in next part of problem).

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \quad K_{\mathrm{a1}} = 4.3 \times 10^{-7}$$

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	$H_2CO_3(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$HCO_3^-(aq)$
Initial (M)	$0.033\ M$	-	0	0
Change (M)	$-x$	-	$+x$	$+x$
Equilibrium (M)	$0.033\ M - x$	-	x	x

Substituting the equilibrium concentrations into the equilibrium constant gives us:

$$K_{H_2CO_3} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Solving the preceding equation making our standard assumptions gives:

$$x = 1.2 \times 10^{-4}$$

Thus:

$$[H_2CO_3] = 0.033\ M$$

$$[H_3O^+] = [HCO_3^-] = 1.2 \times 10^{-4}\ M$$

2. Second Ionization: Determine the concentration of CO_3^{2-} in a solution at equilibrium.

Since the equilibrium step 1 is has a much bigger K_a than equilibrium step 2, we can the equilibrium conditions calculated from first part of example as the initial conditions for an ICER Table for the equilibrium step 2:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

ICER Table for the equilibrium step 2:

ICE Table	$HCO_3^-(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$CO_3^{2-}(aq)$
Initial (M)	$1.2 \times 10^{-4}\ M$	-	$1.2 \times 10^{-4}\ M$	0
Change (M)	$-y$	-	$+y$	$+y$
Equilibrium (M)	$1.2 \times 10^{-4}\ M - y$	-	$1.2 \times 10^{-4}\ M + y$	y

$$K_{HCO_3^-} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]}$$

$$= \frac{(1.2 \times 10^{-4}\ M + y)(y)}{(1.2 \times 10^{-4}\ M - y)}$$

To avoid solving a quadratic equation, we can assume $y \ll 1.2 \times 10^{-4}\ M$ so

$$K_{HCO_3^-} = 4.7 \times 10^{-11} \approx \frac{(1.2 \times 10^{-4}\ M)(y)}{(1.2 \times 10^{-4}\ M)}$$

Rearranging to solve for y

$$y \approx \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4}\ M)}{1.2 \times 10^{-4}\ M}$$

$$[\mathrm{CO_3^{2-}}] = y \approx 4.7 \times 10^{-11}$$

To summarize:

In part 1 of this example, we found that the $\mathrm{H_2CO_3}$ in a 0.033-M solution ionizes slightly and at equilibrium $[\mathrm{H_2CO_3}] = 0.033\ M$, $[\mathrm{H_3O^+}] = 1.2 \times 10^{-4}$, and $[\mathrm{HCO_3^-}] = 1.2 \times 10^{-4}\ M$. In part 2, we determined that $[\mathrm{CO_3^{2-}}] = 5.6 \times 10^{-11}\ M$.

? Exercise 14.7.2: 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 $K_{\mathrm{a1}} = 7.5 \times 10^{-3}$.

- **The second ionization is**

$$\mathrm{H_2PO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HPO_4^{2-}}(aq)$$

with $K_{\mathrm{a2}} = 6.2 \times 10^{-8}$.

- **The third ionization is**

$$\mathrm{HPO_4^{2-}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{PO_4^{3-}}(aq)$$

with $K_{\mathrm{a3}} = 4.2 \times 10^{-13}$.

As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6. This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of 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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14.8: Organic Acids and Bases - Structure and Reactivity

Learning Objectives

- To understand how molecular structure affects the strength of an acid or base.

We have seen that the strengths of acids and bases vary over many orders of magnitude. In this section, we explore some of the structural and electronic factors that control the acidity or basicity of a molecule.

Bond Strengths

In general, the stronger the A– H or B– H^+ bond, the less likely the bond is to break to form H^+ ions and thus the less acidic the substance. This effect can be illustrated using the hydrogen halides:

Relative Acid Strength	HF	HCl	HBr	HI
H–X Bond Energy (kJ/mol)	570	432	366	298
pKa	3.20	−6.1	−8.9	−9.3

The trend in bond energies is due to a steady decrease in overlap between the 1s orbital of hydrogen and the valence orbital of the halogen atom as the size of the halogen increases. The larger the atom to which H is bonded, the weaker the bond. Thus the bond between H and a large atom in a given family, such as I or Te, is weaker than the bond between H and a smaller atom in the same family, such as F or O. As a result, acid strengths of binary hydrides increase as we go down a column of the periodic table. For example, the order of acidity for the binary hydrides of Group 16 elements is as follows, with pK_a values in parentheses:

$$H_2O(14.00 = pK_w) < H_2S(7.05) < H_2Se(3.89) < H_2Te(2.6) \tag{14.8.1}$$

Stability of the Conjugate Base

Whether we write an acid–base reaction as $AH \rightleftharpoons A^- + H^+$ or as $BH^+ \rightleftharpoons B + H^+$, the conjugate base ($A^-$ or B) contains one more lone pair of electrons than the parent acid (AH or BH^+). Any factor that stabilizes the lone pair on the conjugate base favors dissociation of H^+ and makes the parent acid a stronger acid. Let's see how this explains the relative acidity of the binary hydrides of the elements in the second row of the periodic table. The observed order of increasing acidity is the following, with pKa values in parentheses:

$$CH_4(\ 50) \ll NH_3(\ 36) < H_2O(14.00) < HF(3.20) \tag{14.8.2}$$

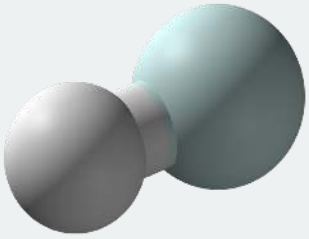
Consider, for example, the compounds at both ends of this series: methane and hydrogen fluoride. The conjugate base of CH_4 is CH_3^-, and the conjugate base of HF is F^-. Because fluorine is much more electronegative than carbon, fluorine can better stabilize the negative charge in the F^- ion than carbon can stabilize the negative charge in the CH3− ion. Consequently, HF has a greater tendency to dissociate to form H^+ and F^- than does methane to form H^+ and CH_3^-, making HF a much stronger acid than CH_4.

The same trend is predicted by analyzing the properties of the conjugate acids. For a series of compounds of the general formula HE, as the electronegativity of E increases, the E–H bond becomes more polar, favoring dissociation to form E^- and H^+. Due to both the increasing stability of the conjugate base and the increasing polarization of the E–H bond in the conjugate acid, acid strengths of binary hydrides increase as we go from left to right across a row of the periodic table.

Acid strengths of binary hydrides increase as we go down a column or from left to right across a row of the periodic table.

the strongest acid Known: The hydrohelium Cation

The storngest 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, HeH^+, which is a positively charged ion formed by the reaction of a proton with a helium atom in the gas phase. It was first produced in the laboratory in 1925 and is isoelectronic with molecular hydrogen (\ce{H2}). It is the strongest known acid, with a proton affinity of 177.8 kJ/mol.



Ball and stick model of the hydrohelium ion. (CC BY-SA 3.0; CCoil).

HeH^+ cannot be prepared in a condensed phase, as it would protonate any anion, molecule or atom with which it were associated. However it is possible to estimate a *hypothetical* aqueous acidity using Hess's law:

$HHe^+(g)$	→	$H^+(g)$	+ He(g)	+178 kJ/mol
$HHe^+(aq)$	→	$HHe^+(g)$		+973 kJ/mol
$H^+(g)$	→	$H^+(aq)$		−1530 kJ/mol
He(g)	→	He(aq)		+19 kJ/mol
$HHe^+(aq)$	→	$H^+(aq)$	+ He(aq)	−360 kJ/mol

A free energy change of dissociation of −360 kJ/mol is equivalent to a pK_a of −63.

It has been suggested that HeH^+ should occur naturally in the interstellar medium, but it has not yet been detected.

Inductive Effects

Atoms or groups of atoms in a molecule other than those to which H is bonded can induce a change in the distribution of electrons within the molecule. This is called an inductive effect, and, much like the coordination of water to a metal ion, it can have a major effect on the acidity or basicity of the molecule. For example, the hypohalous acids (general formula HOX, with X representing a halogen) all have a hydrogen atom bonded to an oxygen atom. In aqueous solution, they all produce the following equilibrium:

$$HOX_{(aq)} \rightleftharpoons H^+_{(aq)} + OX^-(aq) \tag{14.8.3}$$

The acidities of these acids vary by about three orders of magnitude, however, due to the difference in electronegativity of the halogen atoms:

HOX	Electronegativity of X	pKa
HOCl	3.0	7.40
HOBr	2.8	8.55
HOI	2.5	10.5

As the electronegativity of X increases, the distribution of electron density within the molecule changes: the electrons are drawn more strongly toward the halogen atom and, in turn, away from the H in the O–H bond, thus weakening the O–H bond and allowing dissociation of hydrogen as H^+.

The acidity of oxoacids, with the general formula $HOXO_n$ (with n = 0−3), depends strongly on the number of terminal oxygen atoms attached to the central atom X. As shown in Figure 14.8.1, the K_a values of the oxoacids of chlorine increase by a factor of about 10^4 to 10^6 with each oxygen as successive oxygen atoms are added. The increase in acid strength with increasing number of terminal oxygen atoms is due to both an inductive effect and increased stabilization of the conjugate base.

> *Any inductive effect that withdraws electron density from an O–H bond increases the acidity of the compound.*

Because oxygen is the second most electronegative element, adding terminal oxygen atoms causes electrons to be drawn away from the O–H bond, making it weaker and thereby increasing the strength of the acid. The colors in Figure 14.8.1 show how the electrostatic potential, a measure of the strength of the interaction of a point charge at any place on the surface of the molecule, changes as the number of terminal oxygen atoms increases. In Figure 14.8.1 and Figure 14.8.2, blue corresponds to low electron densities, while red corresponds to high electron densities. The oxygen atom in the O–H unit becomes steadily less red from $HClO$ to $HClO_4$ (also written as $HOClO_3$, while the H atom becomes steadily bluer, indicating that the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. The decrease in electron density in the O–H bond weakens it, making it easier to lose hydrogen as H^+ ions, thereby increasing the strength of the acid.

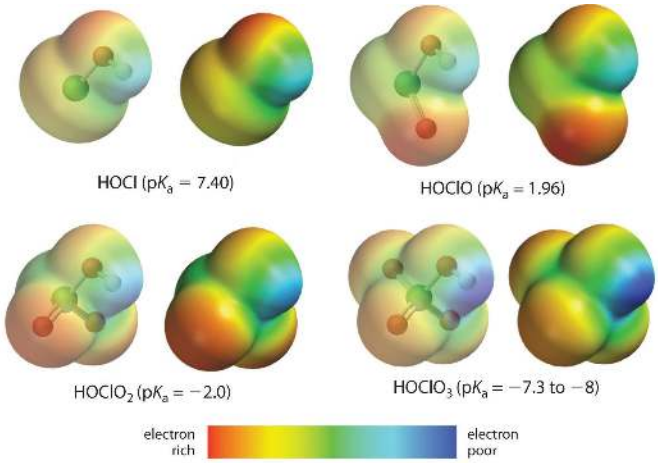
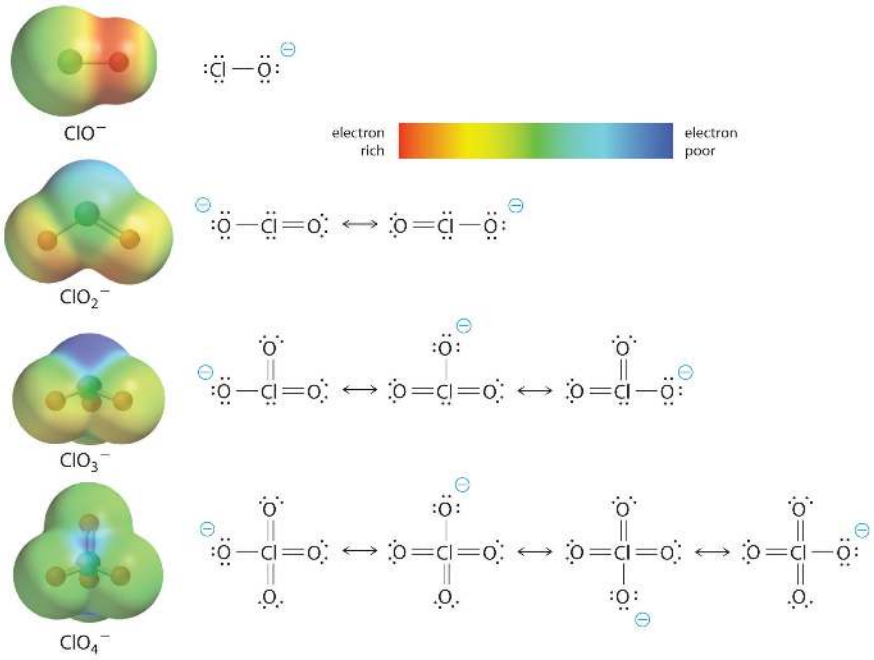


Figure 14.8.1: The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the O–H Unit. These electrostatic potential maps show how the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. Blue corresponds to low electron densities, whereas red corresponds to high electron densities. Source: Chlorine oxoacids pKa values from J. R. Bowser, Inorganic Chemistry (Pacific Grove, CA: Brooks-Cole,1993).

At least as important, however, is the effect of delocalization of the negative charge in the conjugate base. As shown in Figure 14.8.2, the number of resonance structures that can be written for the oxoanions of chlorine increases as the number of terminal oxygen atoms increases, allowing the single negative charge to be delocalized over successively more oxygen atoms.

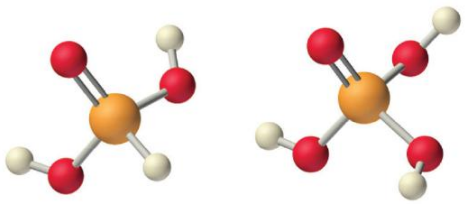
Electron delocalization in the conjugate base increases acid strength.

The electrostatic potential plots in Figure 14.8.2 demonstrate that the electron density on the terminal oxygen atoms decreases steadily as their number increases. The oxygen atom in ClO^- is red, indicating that it is electron rich, and the color of oxygen progressively changes to green in ClO_4^+, indicating that the oxygen atoms are becoming steadily less electron rich through the series. For example, in the perchlorate ion (ClO_4^-), the single negative charge is delocalized over all four oxygen atoms, whereas in the hypochlorite ion (OCl^-), the negative charge is largely localized on a single oxygen atom (Figure 14.8.2). As a result, the perchlorate ion has no localized negative charge to which a proton can bind. Consequently, the perchlorate anion has a much lower affinity for a proton than does the hypochlorite ion, and perchloric acid is one of the strongest acids known.



As the number of terminal oxygen atoms increases, the number of resonance structures that can be written for the oxoanions of chlorine also increases, and the single negative charge is delocalized over more oxygen atoms. As these electrostatic potential plots demonstrate, the electron density on the terminal oxygen atoms decreases steadily as their number increases. As the electron density on the oxygen atoms decreases, so does their affinity for a proton, making the anion less basic. As a result, the parent oxoacid is more acidic.

Similar inductive effects are also responsible for the trend in the acidities of oxoacids that have the same number of oxygen atoms as we go across a row of the periodic table from left to right. For example, H_3PO_4 is a weak acid, H_2SO_4 is a strong acid, and $HClO_4$ is one of the strongest acids known. The number of terminal oxygen atoms increases steadily across the row, consistent with the observed increase in acidity. In addition, the electronegativity of the central atom increases steadily from P to S to Cl, which causes electrons to be drawn from oxygen to the central atom, weakening the O–H bond and increasing the strength of the oxoacid.



Careful inspection of the data in Table 14.8.1 shows two apparent anomalies: carbonic acid and phosphorous acid. If carbonic acid (H_2CO_3) were a discrete molecule with the structure $(HO)_2C{=}O$, 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 $(HO)_2P(=O)H$ with one H atom directly bonded to P and one P=O bond. Thus the pKa1 for phosphorous acid is similar to that of other oxoacids with one terminal oxygen atom, such as H_3PO_4. Fortunately, phosphorous acid is the only common oxoacid in which a hydrogen atom is bonded to the central atom rather than oxygen.

Table 14.8.1: Values of pKa for Selected Polyprotic Acids and Bases

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Polyprotic Acids	Formula	pK_{a1}	pK_{a2}	pK_{a3}
carbonic acid*	"H_2CO_3"	6.35	10.33	
citric acid	$HO_2CCH-2C(OH)(CO_2H)CH_2CO_2H$	3.13	4.76	6.40
malonic acid	$HO-2CCH_2CO_2H$	2.85	5.70	
oxalic acid	HO_2CCO_2H	1.25	3.81	
phosphoric acid	H_3PO_4	2.16	7.21	12.32
phosphorous acid	H_3PO_3	1.3	6.70	
succinic acid	$HO_2CCH_2CH_2CO_2H$	4.21	5.64	
sulfuric acid	H_2SO_4	−2.0	1.99	
sulfurous acid*	"H_2SO_3"	1.85	7.21	
Polyprotic Bases	**Formula**	pK_{b1}	pK_{b2}	
ethylenediamine	$H_2N(CH_2)_2NH_2$	4.08	7.14	
piperazine	$HN(CH_2CH_2)_2NH$	4.27	8.67	
propylenediamine	$H_2N(CH_2)_3NH_2$	3.45	5.12	

*H_2CO_3 and H_2SO_3 are at best minor components of aqueous solutions of $CO_{2(g)}$ and $SO_{2(g)}$, respectively, but such solutions are commonly referred to as containing carbonic acid and sulfurous acid, respectively.

Inductive effects are also observed in organic molecules that contain electronegative substituents. The magnitude of the electron-withdrawing effect depends on both the nature and the number of halogen substituents, as shown by the pKa values for several acetic acid derivatives:

$$pK_aCH_3CO_2H4.76 < CH_2ClCO_2H2.87 < CHCl_2CO_2H1.35 < CCl_3CO_2H0.66 < CF_3CO_2H0.52$$

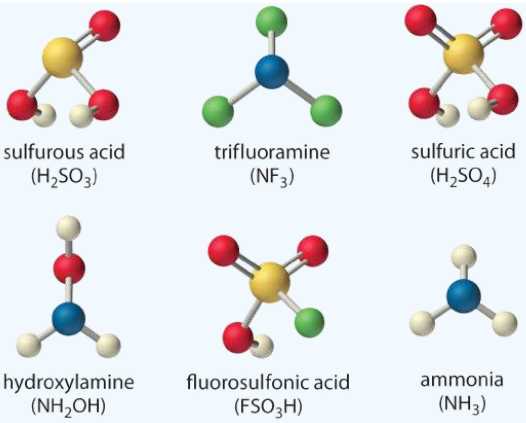
As you might expect, fluorine, which is more electronegative than chlorine, causes a larger effect than chlorine, and the effect of three halogens is greater than the effect of two or one. Notice from these data that inductive effects can be quite large. For instance, replacing the $-CH_3$ group of acetic acid by a $-CF_3$ group results in about a 10,000-fold increase in acidity!

Example 14.8.1

Arrange the compounds of each series in order of increasing acid or base strength.

a. sulfuric acid [H_2SO_4, or $(HO)_2SO_2$], fluorosulfonic acid (FSO_3H, or FSO_2OH), and sulfurous acid [H_2SO_3, or $(HO)_2SO$]
b. ammonia (NH_3), trifluoramine (NF_3), and hydroxylamine (NH_2OH)

The structures are shown here.



Given: series of compounds

Asked for: relative acid or base strengths

Strategy:

Use relative bond strengths, the stability of the conjugate base, and inductive effects to arrange the compounds in order of increasing tendency to ionize in aqueous solution.

Solution:

Although both sulfuric acid and sulfurous acid have two –OH groups, the sulfur atom in sulfuric acid is bonded to two terminal oxygen atoms versus one in sulfurous acid. Because oxygen is highly electronegative, sulfuric acid is the stronger acid because the negative charge on the anion is stabilized by the additional oxygen atom. In comparing sulfuric acid and fluorosulfonic acid, we note that fluorine is more electronegative than oxygen. Thus replacing an –OH by –F will remove more electron density from the central S atom, which will, in turn, remove electron density from the S–OH bond and the O–H bond. Because its O–H bond is weaker, FSO_3H is a stronger acid than sulfuric acid. The predicted order of acid strengths given here is confirmed by the measured pKa values for these acids:

$$pKaH_2SO_31.85 < H_2SO_4^{-2} < FSO_3H - 10$$

The structures of both trifluoramine and hydroxylamine are similar to that of ammonia. In trifluoramine, all of the hydrogen atoms in NH3 are replaced by fluorine atoms, whereas in hydroxylamine, one hydrogen atom is replaced by OH. Replacing the three hydrogen atoms by fluorine will withdraw electron density from N, making the lone electron pair on N less available to bond to an H^+ ion. Thus NF_3 is predicted to be a much weaker base than NH_3. Similarly, because oxygen is more electronegative than hydrogen, replacing one hydrogen atom in NH_3 by OH will make the amine less basic. Because oxygen is less electronegative than fluorine and only one hydrogen atom is replaced, however, the effect will be smaller. The predicted order of increasing base strength shown here is confirmed by the measured pK_b values:

$$pK_bNF_3 — << NH_2OH8.06 < NH_34.75$$

Trifluoramine is such a weak base that it does not react with aqueous solutions of strong acids. Hence its base ionization constant has never been measured.

? Exercise 14.8.1

Arrange the compounds of each series in order of

a. decreasing acid strength: H_3PO_4, $CH_3PO_3H_2$, and $HClO_3$.
b. increasing base strength: CH_3S^-, OH^-, and CF_3S^-.

Answer a

$HClO-3 > CH_3PO_3H_2 > H_3PO_4$

Answer a

$CF_3S^- < CH_3S^- < OH^-$

Summary

Inductive effects and charge delocalization significantly influence the acidity or basicity of a compound. The acid–base strength of a molecule depends strongly on its structure. The weaker the A–H or B–H+ bond, the more likely it is to dissociate to form an H^+ ion. In addition, any factor that stabilizes the lone pair on the conjugate base favors the dissociation of H^+, making the conjugate acid a stronger acid. Atoms or groups of atoms elsewhere in a molecule can also be important in determining acid or base strength through an inductive effect, which can weaken an O– H bond and allow hydrogen to be more easily lost as H^+ ions.

Contributors and Attributions

- Anonymous

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14.9: A Deeper Look - Exact Treatment of Acid-Base Equilibria

Learning Objectives

- Calculate the pH when two weak acids are present in a solution.
- Calculate the pH when the concentration of the acid is very dilute.
- Calculate the pH by including the autoionization of water.

A common paradigm in solving for pHs in weak acids and bases is that the equilibria of solutions containing one weak acid or one weak base. In most cases, the amount of H^+ from the autoionization of water is negligible. For very dilute solutions, the amount of H^+ ions from the autoionization of water must also be taken into account. Thus, a strategy is given here to deal with these systems.

When two or more acids are present in a solution, the concentration of H^+ (or pH) of the solution depends on the concentrations of the acids and their acidic constants K_a. The hydrogen ion is produced by the ionization of all acids, but the ionizations of the acids are governed by their equilibrium constants, K_a's. Similarly, the concentration of OH^- ions in a solution containing two or more weak bases depends on the concentrations and K_b values of the bases. For simplicity, we consider two acids in this module, but the strategies used to discuss equilibria of two acids apply equally well to that of two bases.

Dissociation of Acids and Bases in Water Couple Two Equilibria with a Common Ion H^+

If the pH is between 6 and 8, the contribution due to autoionization of water to $[H^+]$ should also be considered. When autoionization of water is considered, the method is called the **exact pH calculation** or the **exact treatment**. This method is illustrated below. When the contribution of pH due to self-ionization of water cannot be neglected, there are two coupled equilibria to consider:

$$HA \rightleftharpoons H^+ + A^- \tag{14.9.1}$$

ICE Table	HA	H^+	A^-
Initial	C	0	0
Change	$-x$	x	x
Equilibrium	$C-x$	x	x

and

$$H_2O \rightleftharpoons H^+ + OH^- \tag{14.9.2}$$

ICE Table	H_2O	H^+	OH^-
Equilibrium	-	y	y

Thus,

$$[H^+] = (x+y) \tag{14.9.3}$$
$$[A^-] = x \tag{14.9.4}$$
$$[OH^-] = y \tag{14.9.5}$$

and the two equilibrium constants are

$$K_a = \frac{(x+y)\,x}{C-x} \tag{14.9.6}$$

and

$$K_w = (x+y)\,y \tag{14.9.7}$$

Although you may use the method of successive approximation, the formula to calculate the pH can be derived directly from Equations 14.9.6 and 14.9.7. Solving for x from Equation 14.9.7 gives

$$x = \frac{K_w}{y} - y \tag{14.9.8}$$

and substituting this expression into 14.9.6 results in

$$K_a = \frac{(x+y)\left(\frac{K_w}{y} - y\right)}{C - \frac{K_w}{y} + y} \tag{14.9.9}$$

Rearrange this equation to give:

$$[H^+] = (x+y) \tag{14.9.10}$$

$$= \frac{C - \frac{K_w}{y} + y}{\frac{K_w}{y} - y} K_a \tag{14.9.11}$$

Note that

$$\frac{K_w}{y} = [H^+] \tag{14.9.12}$$

so

$$y = \frac{K_w}{[H^+]}. \tag{14.9.13}$$

Thus, we get:

$$[H^+] = \frac{C - [H^+] + \frac{K_w}{[H^+]}}{[H^+] - \frac{K_w}{[H^+]}} K_a \tag{14.9.14}$$

As written, Equation 14.9.14 is complicated, but can be put into a polynomial form

$$[H^+]^3 + K_a[H^+]^2 - (K_w + CK_a)[H^+] - K_wK_a = 0 \tag{14.9.15}$$

Solving for the exact hydronium concentration requires solving a third-order polynomial. While this is analytically feasible, it is an awkward equation to handle. Instead, we often consider two approximations to Equation 14.9.15 that can made under limiting conditions.

Case 1: High Concentration Approximation

If $[H^+] > 1 \times 10^{-6}$, then

$$\frac{K_w}{[H^+]} < 1 \times 10^{-8}. \tag{14.9.16}$$

This is small indeed compared to $[H^+]$ and C in Equation 14.9.14 Thus,

$$[H^+] \approx \frac{C - [H^+]}{[H^+]} K_a \tag{14.9.17}$$

$$[H^+]^2 + K_a[H^+] - CK_a \approx 0 \tag{14.9.18}$$

Equation 14.9.18 is a quadratic equation with two solutions. However, only one will be positive and real:

$$[H^+] \approx \frac{-K_a + \sqrt{K_a^2 + 4CK_a}}{2} \tag{14.9.19}$$

Case 2: Low Concentration Approximation

If $[H^+] \ll C$, then

$$C - [H^+] \approx C \tag{14.9.20}$$

Equation 14.9.14 can be simplified

$$[H^+] \approx \frac{C}{[H^+]}\, K_\text{a} \tag{14.9.21}$$

$$[H^+] \approx \sqrt{CK_\text{a}} \tag{14.9.22}$$

The treatment presented in deriving Equation 14.9.14 is more general, and may be applied to problems involving two or more weak acids in one solution.

Example 14.9.1

Calculate the $[\text{H}^+]$, $[\text{Ac}^-]$, and $[\text{Cc}^-]$ when the solution contains 0.200 M HAc ($K_a = 1.8 \times 10^{-5}$), and 0.100 M HCc (the acidity constant $K_c = 1.4 \times 10^{-3}$). (HAc is acetic acid whereas HCc is chloroacetic acid).

Solution

Assume x and y to be the concentrations of Ac^- and Cc^-, respectively, and write the concentrations below the equations:

$$\begin{array}{ccccc} \text{HAc} & \rightleftharpoons & \text{H}^+ & + & \text{Ac}^- \\ 0.200 - x & & x & & x \end{array}$$

$$\begin{array}{ccccc} \text{HCc} & \rightleftharpoons & \text{H}^+ & + & \text{Cc}^- \\ 0.100 - y & & y & & y \end{array}$$

$$[\text{H}^+] = (x + y)$$

Thus, you have

$$\frac{(x+y)\,x}{0.200 - x} = 1.8 \times 10^{-5} \tag{14.9.23}$$

$$\frac{(x+y)\,y}{0.100 - y} = 1.4 \times 10^{-3} \tag{14.9.24}$$

Solving for x and y from Equations 14.9.23 and 14.9.24 may seem difficult, but you can often make some assumptions to simplify the solution procedure. Since HAc is a weaker acid than is HCc, you expect x << y. Further, y << 0.100. Therefore, $x + y \approx y$ and 0.100 - y => 0.100. Equation 14.9.24 becomes:

$$\frac{(y)\,y}{0.100} = 1.4 \times 10^{-3} \tag{14.9.25}$$

which leads to

$$\begin{aligned} y &= (1.4 \times 10^{-3} \times 0.100)^{1/2} \\ &= 0.012 \end{aligned}$$

Substituting y in Equation 14.9.23 results in

$$\frac{(x + 0.012)\,x}{0.200 - x} = 1.8 \times 10^{-5} \tag{14.9.26}$$

This equation is easily solved, but you may further assume that $0.200 - x \approx 0.200$, since $x << 0.200$. Thus,

$$\begin{aligned} x &= \frac{-0.012 + (1.44 \times 10^{-4} + 1.44 \times 10^{-5})^{1/2}}{2} \\ &= 2.9 \times 10^{-4} \quad \longleftarrow \text{Small indeed compared to } 0.200 \end{aligned}$$

You had a value of 0.012 for y by neglecting the value of x in Equation 14.9.24 You can now recalculate the value for y by substituting values for x and y in Equation 14.9.24

$$\frac{(2.9\times10^{-4}+y)\,y}{0.100-0.012}=1.4\times10^{-3} \tag{14.9.27}$$

Solving for y in the above equation gives

$$y=0.011$$

You have improved the y value from 0.012 to 0.011. Substituting the new value for y in a successive approximation to recalculate the value for x improves its value from 2.9×10^{-4} to a new value of 3.2×10^{-4}. Use your calculator to obtain these values. Further refinement does not lead to any significant changes for x or y.

Discussion

You should write down these calculations on your note pad, since reading alone does not lead to thorough understanding.

Example 14.9.2

A weak acid HA has a K_a value of 4.0×10^{-11}. What are the pH and the equilibrium concentration of A^- in a solution of 0.0010 M HA?

Solution

For the solution of this problem, two methods are given here. If you like the x and y representation, you may use method (a).

Method (a)

The two equilibrium equations are:

$$\begin{array}{ccccc} HA & \rightleftharpoons & H^+ & + & A^-; \\ 0.0010-x & & x & & x \end{array} \tag{14.9.28}$$

$$\begin{array}{ccccc} H_2O & \rightleftharpoons & H^+ & + & OH^- \\ & & y & & y \end{array}$$

$$[H^+]=(x+y) \tag{14.9.29}$$

$$\frac{(x+y)\,x}{0.0010-x}=4.0\times10^{-}11 \tag{14.9.30}$$

(14.9.31)

$$(x+y)\,y=1\times10^{-}14 \tag{14.9.32}$$

Assume y << x, and x << 0.0010, then you have

$$\frac{(x)\,x}{0.0010}=4.0\times10^{-11} \tag{14.9.33}$$

$$x=(0.0010\times4.0e^{-11})^{1/2} \tag{14.9.34}$$

$$=2.0\times10^{-7} \tag{14.9.35}$$

Substituting $2.0\times^{-7}$ for x in 4 and solving the quadratic equation for y gives,

$$(2.0\times10^{-}7+y)\,y=1\times10^{-14}$$

$$y=4.1\times10^{-8}$$

Substituting 4.1×10^{-8} in Equation 14.9.30, but still approximating 0.0010-x by 0.0010:

$$\frac{(x+4.1\times10^{-8})\,x}{0.0010}=4.0\times10^{-11} \tag{14.9.36}$$

Solving this quadratic equation for a positive root results in

$$x = 1.8 \times 10^{-7}\ \text{M} \longleftarrow \text{Recall } x = [\text{A}^-]$$

$$\begin{aligned}[\text{H}^+] &= x + y \\ &= (1.8 + 0.41)\, 1 \times 10^{-7} \\ &= 2.2 \times 10^{-7} \\ \text{pH} &= 6.65\end{aligned}$$

The next method uses the formula derived earlier.

Method (b)

Using the formula from the exact treatment, and using 2×10^{-7} for all the $[\text{H}^+]$ values on the right hand side, you obtain a new value of $[\text{H}^+]$ on the left hand side,

$$\begin{aligned}[\text{H}^+] &= \frac{C - [\text{H}^+] + \dfrac{K_\text{w}}{[\text{H}^+]}}{[\text{H}^+] - \dfrac{K_\text{w}}{[\text{H}^+]}} K_\text{a} \\ &= 2.24 \times 10^{-7} \\ \text{pH} &= 6.65\end{aligned}$$

The new $[\text{H}^+]$ enables you to recalculate $[\text{A}^-]$ from the formula:

$$\begin{aligned}(2.24 \times 10^{-7})[\text{A}^-] &= CK_\text{a} \\ [\text{A}^-] &= \frac{(0.0010)(4.0 \times 10^{-11})}{2.24 \times 10^{-7}} \\ &= 1.8 \times 10^{-7}\end{aligned}$$

DISCUSSION

You may have attempted to use the approximation method:

$$\begin{aligned}x &= (CK_\text{a})^{1/2} \\ &= 2.0 \times 10^{-7}\ \text{M A}^-,\ \text{or H}^+;\ \text{pH} = 6.70\end{aligned}$$

and obtained a pH of 6.70, which is greater than 6.65 by less than 1%. However, when an approximation is made, you have no confidence in the calculated pH of 6.70.

Summary

Water is both an acid and a base due to the autoionization,

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$$

However, the amount of H^+ ions from water may be very small compared to the amount from an acid if the concentration of the acid is high. When calculating $[\text{H}^+]$ in an acidic solution, approximation method or using the quadratic formula has been discussed in the modules on weak acids.

Contributors and Attributions

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14.10: Precipitation and Dissolution

Learning Objectives

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

- Write chemical equations and equilibrium expressions representing solubility equilibria
- Carry out equilibrium computations involving solubility, equilibrium expressions, and solute concentrations

Solubility equilibria are established when the dissolution and precipitation of a solute species occur at equal rates. These equilibria underlie many natural and technological processes, ranging from tooth decay to water purification. An understanding of the factors affecting compound solubility is, therefore, essential to the effective management of these processes. This section applies previously introduced equilibrium concepts and tools to systems involving dissolution and precipitation.

The Solubility Product

Recall from the chapter on solutions that the solubility of a substance can vary from essentially zero (*insoluble* or *sparingly soluble*) to infinity (*miscible*). A solute with finite solubility can yield a *saturated* solution when it is added to a solvent in an amount exceeding its solubility, resulting in a heterogeneous mixture of the saturated solution and the excess, undissolved solute. For example, a saturated solution of silver chloride is one in which the equilibrium shown below has been established.

$$\mathrm{AgCl(s)} \underset{\text{precipitation}}{\overset{\text{dissolution}}{\rightleftharpoons}} \mathrm{Ag^+(aq) + Cl^-(aq)}$$

In this solution, an excess of solid AgCl dissolves and dissociates to produce aqueous $\mathrm{Ag^+}$ and $\mathrm{Cl^-}$ ions at the same rate that these aqueous ions combine and precipitate to form solid AgCl (Figure 14.10.1). Because silver chloride is a sparingly soluble salt, the equilibrium concentration of its dissolved ions in the solution is relatively low.

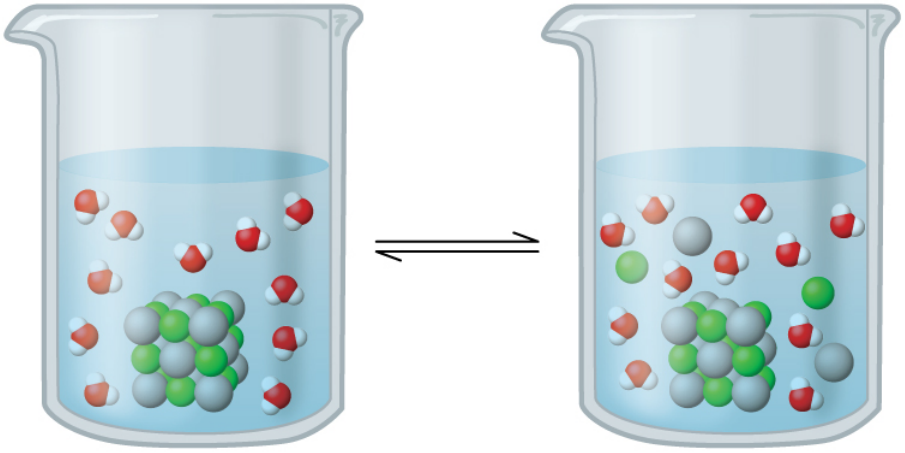


Figure 14.10.1: Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of $\mathrm{Ag^+}$ and $\mathrm{Cl^-}$ ions in equilibrium with undissolved silver chloride.

The equilibrium constant for solubility equilibria such as this one is called the **solubility product constant, K_{sp}**, in this case

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

Recall that only gases and solutes are represented in equilibrium constant expressions, so the K_{sp} does not include a term for the undissolved AgCl. A listing of solubility product constants for several sparingly soluble compounds is provided in Appendix J.

Example 14.10.1: Writing Equations and Solubility Products

Write the dissolution equation and the solubility product expression for each of the following slightly soluble ionic compounds:

a. AgI, silver iodide, a solid with antiseptic properties
b. $CaCO_3$, calcium carbonate, the active ingredient in many over-the-counter chewable antacids

c. $Mg(OH)_2$, magnesium hydroxide, the active ingredient in Milk of Magnesia
d. $Mg(NH_4)PO_4$, magnesium ammonium phosphate, an essentially insoluble substance used in tests for magnesium
e. $Ca_5(PO_4)_3OH$, the mineral apatite, a source of phosphate for fertilizers

Solution

a. $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$

$$K_{sp} = [Ag^+]\,[I^-]$$

b. $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$

$$K_{sp} = [Ca^{2+}]\,[CO_3^{2-}]$$

c. $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)$

$$K_{sp} = [Mg^{2+}]\,[OH^-]^2$$

d. $Mg(NH_4)PO_4(s) \rightleftharpoons Mg^{2+}(aq) + NH_4^+(aq) + PO_4^{3-}(aq)$

$$K_{sp} = [Mg^{2+}]\,[NH_4^+]\,[PO_4^{3-}]$$

e. $Ca_5(PO_4)3\,OH(s) \rightleftharpoons 5\,Ca^{2+}(aq) + 3\,PO_4^{3-}(aq) + OH^-(aq)$

$$K_{sp} = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-]$$

? Exercise 14.10.1

Write the dissolution equation and the solubility product for each of the following slightly soluble compounds:

a. $BaSO_4$
b. Ag_2SO_4
c. $Al(OH)_3$
d. Pb(OH)Cl

Answer

a. $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

b. $Ag_2SO_4(s) \rightleftharpoons 2\,Ag^+(aq) + SO_4^{2-}(aq)$

$$K_{sp} = [Ag^+]^2\,[SO_4^{2-}]$$

c. $Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3\,OH^-(aq)$

$$K_{sp} = [Al^{3+}]\,[OH^-]^3$$

d. $Pb(OH)Cl(s) \rightleftharpoons Pb^{2+}(aq) + OH^-(aq) + Cl^-(aq)$

$$K_{sp} = [Pb^{2+}]\,[OH^-]\,[Cl^-]$$

K_{sp} and Solubility

The K_{sp} of a slightly soluble ionic compound may be simply related to its measured solubility provided the dissolution process involves only dissociation and solvation, for example:

$$M_pX_q(s) \rightleftharpoons p\,M^{m+}(aq) + q\,X^{n-}(aq)$$

For cases such as these, one may derive K_{sp} values from provided solubilities, or vice-versa. Calculations of this sort are most conveniently performed using a compound's molar solubility, measured as moles of dissolved solute per liter of saturated solution.

Example 14.10.2: Calculation of K_{sp} from Equilibrium Concentrations

Fluorite, CaF_2, is a slightly soluble solid that dissolves according to the equation:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

The concentration of Ca^{2+} in a saturated solution of CaF_2 is 2.15×10^{-4} M. What is the solubility product of fluorite?

Solution

According to the stoichiometry of the dissolution equation, the fluoride ion molarity of a CaF_2 solution is equal to twice its calcium ion molarity:

$$\left[F^-\right] = \left(2 \text{ mol } F^-/1 \text{ mol } Ca^{2+}\right) = (2)\left(2.15 \times 10^{-4} M\right) = 4.30 \times 10^{-4} M$$

Substituting the ion concentrations into the K_{sp} expression gives

$$K_{sp} = \left[Ca^{2+}\right]\left[F^-\right]^2 = \left(2.15 \times 10^{-4}\right)\left(4.30 \times 10^{-4}\right)^2 = 3.98 \times 10^{-11}$$

Exercise 14.10.2

In a saturated solution of $Mg(OH)_2$, the concentration of Mg^{2+} is 1.31×10^{-4} M. What is the solubility product for $Mg(OH)_2$?

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)$$

Answer

8.99×10^{-12}

Example 14.10.3: Determination of Molar Solubility from K_{sp}

The K_{sp} of copper(I) bromide, CuBr, is 6.3×10^{-9}. Calculate the molar solubility of copper bromide.

Solution

The dissolution equation and solubility product expression are

$$CuBr(s) \rightleftharpoons Cu^+(aq) + Br^-(aq)$$

with

$$K_{sp} = \left[Cu^+\right]\left[Br^-\right]$$

Following the ICE approach to this calculation yields the table

	CuBr (s) $\rightleftharpoons$ Cu^+ (*aq*) + Br^- (*aq*)		
Initial concentration (*M*)		0	0
Change (*M*)		+*x*	+*x*
Equilibrium concentration (*M*)		*x*	*x*

Substituting the equilibrium concentration terms into the solubility product expression and solving for *x* yields

$$\begin{aligned} K_{sp} &= \left[Cu^+\right]\left[Br^-\right] \\ 6.3 \times 10^{-9} &= (x)(x) = x^2 \\ x &= \sqrt{6.3 \times 10^{-9}} \\ &= 7.9 \times 10^{-5} \text{ M} \end{aligned}$$

Since the dissolution stoichiometry shows one mole of copper(I) ion and one mole of bromide ion are produced for each moles of Br dissolved, the molar solubility of CuBr is $7.9 \times 10^{-5}\ \text{M}$.

Exercise 14.10.3

The K_{sp} of AgI is 1.5×10^{-16}. Calculate the molar solubility of silver iodide.

Answer

$1.2 \times 10^{-8}\ \text{M}$

Example 14.10.4: Determination of Molar Solubility from K_{sp}

The K_{sp} of calcium hydroxide, $Ca(OH)_2$, is 1.3×10^{-6}. Calculate the molar solubility of calcium hydroxide.

Solution

The dissolution equation and solubility product expression are

$$\text{Ca(OH)}_2\text{(s)} \rightleftharpoons \text{Ca}^{2+}\text{(aq)} + 2\,\text{OH}^-\text{(aq)}$$

with

$$K_{sp} = \left[\text{Ca}^{2+}\right]\left[\text{OH}^-\right]^2$$

The ICE table for this system is

	$Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq)$	+	$2OH^-\,(aq)$
Initial concentration (*M*)		0	0
Change (*M*)		+*x*	+2*x*
Equilibrium concentration (*M*)		*x*	2*x*

Substituting terms for the equilibrium concentrations into the solubility product expression and solving for x gives

$$\begin{aligned} K_{sp} &= \left[\text{Ca}^{2+}\right]\left[\text{OH}^-\right]^2 \\ 1.3 \times 10^{-6} &= (x)(2x)^2 = (x)\left(4x^2\right) = 4x^3 \\ x &= \sqrt[3]{\frac{1.3 \times 10^{-6}}{4}} \\ &= 6.9 \times 10^{-3}\ \text{M} \end{aligned}$$

As defined in the ICE table, x is the molarity of calcium ion in the saturated solution. The dissolution stoichiometry shows a 1:1 relation between moles of calcium ion in solution and moles of compound dissolved, and so, the molar solubility of $Ca(OH)_2$ is $6.9 \times 10^{-3}\ \text{M}$.

Exercise 14.10.4

The K_{sp} of PbI_2 is 1.4×10^{-8}. Calculate the molar solubility of lead(II) iodide.

Answer

$1.5 \times 10^{-3}\ \text{M}$

Example 14.10.5: Determination of K_{sp} from Gram Solubility

Many of the pigments used by artists in oil-based paints (Figure 14.10.2) are sparingly soluble in water. For example, the solubility of the artist's pigment chrome yellow, $PbCrO_4$, is 4.6×10^{-6} g/L. Determine the solubility product for $PbCrO_4$.



Figure 14.10.2: Oil paints contain pigments that are very slightly soluble in water. In addition to chrome yellow ($PbCrO_4$), examples include Prussian blue ($Fe_7(CN)_{18}$), the reddish-orange color vermilion (HgS), and green color veridian (Cr_2O_3). (credit: Sonny Abesamis)

Solution

Before calculating the solubility product, the provided solubility must be converted to molarity:

$$[\mathrm{PbCrO_4}] = \frac{4.6 \times 10^{-6}\ \mathrm{g\ PbCrO4}}{1\ \mathrm{L}} \times \frac{1\ \mathrm{mol\ PbCrO_4}}{323.2\ \mathrm{g\ PbCrO_4}}$$

$$= \frac{1.4 \times 10^{-8}\ \mathrm{mol\ PbCrO_4}}{1\ \mathrm{L}}$$

$$= 1.4 \times 10^{-8}\ \mathrm{M}$$

The dissolution equation for this compound is

$$\mathrm{PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)}$$

The dissolution stoichiometry shows a 1:1 relation between the molar amounts of compound and its two ions, and so both $[\mathrm{Pb^{2+}}]$ and $[\mathrm{CrO_4^{2-}}]$ are equal to the molar solubility of $\mathrm{PbCrO_4}$:

$$[\mathrm{Pb^{2+}}] = [\mathrm{CrO_4^{2-}}] = 1.4 \times 10^{-8}\ \mathrm{M}$$

Therefore

$$K_{sp} = [\mathrm{Pb^{2+}}][\mathrm{CrO_4^{2-}}] = (1.4 \times 10^{-8})(1.4 \times 10^{-8}) = 2.0 \times 10^{-16}$$

Exercise 14.10.5

The solubility of TlCl [thallium(I) chloride], an intermediate formed when thallium is being isolated from ores, is 3.12 grams per liter at 20 °C. What is its solubility product?

Answer

1.69×10^{-4}

Example 14.10.6: Calculating the Solubility of Hg_2Cl_2

Calomel, Hg_2Cl_2, is a compound composed of the diatomic ion of mercury(I), and chloride ions, Cl^-. Although most mercury compounds are now known to be poisonous, eighteenth-century physicians used calomel as a medication. Their patients rarely

suffered any mercury poisoning from the treatments because calomel has a very low solubility, as suggested by its very small K_{sp}:

$$\mathrm{Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\,Cl^-(aq)} \quad K_{sp} = 1.1 \times 10^{-18}$$

Calculate the molar solubility of $\mathrm{Hg_2Cl_2}$.

Solution

The dissolution stoichiometry shows a 1:1 relation between the amount of compound dissolved and the amount of mercury(I) ions, and so the molar solubility of Hg_2Cl_2 is equal to the concentration of ions

Following the ICE approach results in

	$Hg_2Cl_2\,(s) \rightleftharpoons Hg_2^{2+}\,(aq)$	+	$2Cl^-\,(aq)$
Initial concentration (*M*)		0	0
Change (*M*)		$+x$	$+2x$
Equilibrium concentration (*M*)		x	$2x$

Substituting the equilibrium concentration terms into the solubility product expression and solving for x gives

$$\begin{aligned} K_{sp} &= \left[\mathrm{Hg_2^{2+}}\right]\left[\mathrm{Cl^-}\right]^2 \\ 1.1 \times 10^{-18} &= (x)(2x)^2 \\ 4x^3 &= 1.1 \times 10^{-18} \\ x &= \sqrt[3]{\left(\frac{1.1 \times 10^{-18}}{4}\right)} \\ &= 6.5 \times 10^{-7}\ \mathrm{M} \end{aligned}$$

Therefore

$$\begin{aligned} \left[\mathrm{Hg_2^{2+}}\right] &= 6.5 \times 10^{-7}\ \mathrm{M} \\ &= 6.5 \times 10^{-7}\ \mathrm{M} \\ \left[\mathrm{Cl^-}\right] &= 2x = 2\left(6.5 \times 10^{-7}\ \mathrm{M}\right) \\ &= 1.3 \times 10^{-6} M \end{aligned}$$

The dissolution stoichiometry shows the molar solubility of $\mathrm{Hg_2Cl_2}$ is equal to $\left[\mathrm{Hg_2^{2+}}\right]$ or $6.5 \times 10^{-7}\ \mathrm{M}$.

? Exercise 14.10.6

Determine the molar solubility of MgF_2 from its solubility product: $K_{sp} = 6.4 \times 10^{-9}$.

Answer

$1.2 \times 10^{-3}\ \mathrm{M}$

How Sciences Interconnect: Using Barium Sulfate for Medical Imaging

Various types of medical imaging techniques are used to aid diagnoses of illnesses in a noninvasive manner. One such technique utilizes the ingestion of a barium compound before taking an X-ray image. A suspension of barium sulfate, a chalky powder, is ingested by the patient. Since the K_{sp} of barium sulfate is 2.3×10^{-8}, very little of it dissolves as it coats the lining of the patient's intestinal tract. Barium-coated areas of the digestive tract then appear on an X-ray as white, allowing for greater visual detail than a traditional X-ray (Figure 14.10.3).



Figure 14.10.3: A suspension of barium sulfate coats the intestinal tract, permitting greater visual detail than a traditional X-ray. (credit modification of work by “glitzy queen00”/Wikimedia Commons)

Medical imaging using barium sulfate can be used to diagnose acid reflux disease, Crohn’s disease, and ulcers in addition to other conditions.

Visit this website for more information on how barium is used in medical diagnoses and which conditions it is used to diagnose.

Predicting Precipitation

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

$$\mathrm{CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)}$$

with

$$K_{sp} = \left[\mathrm{Ca^{2+}}\right]\left[\mathrm{CO_3^{2-}}\right] = 8.7 \times 10^{-9}$$

It is important to realize that this equilibrium is established in any aqueous solution containing Ca^{2+} and CO_3^{2-} ions, not just in a solution formed by saturating water with calcium carbonate. Consider, for example, mixing aqueous solutions of the soluble compounds sodium carbonate and calcium nitrate. If the concentrations of calcium and carbonate ions in the mixture do not yield a reaction quotient, Q_{sp}, that exceeds the solubility product, K_{sp}, then no precipitation will occur. If the ion concentrations yield a reaction quotient greater than the solubility product, then precipitation will occur, lowering those concentrations until equilibrium is established ($Q_{sp} = K_{sp}$). The comparison of Q_{sp} to K_{sp} to predict precipitation is an example of the general approach to predicting the direction of a reaction first introduced in the chapter on equilibrium. For the specific case of solubility equilibria:

- $Q_{sp} < K_{sp}$: the reaction proceeds in the forward direction (solution is not saturated; no precipitation observed)
- $Q_{sp} > K_{sp}$: the reaction proceeds in the reverse direction (solution is supersaturated; precipitation will occur)

This predictive strategy and related calculations are demonstrated in the next few example exercises.

Example 14.10.7: Precipitation of $Mg(OH)_2$

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of lime, $Ca(OH)_2$, a readily available inexpensive source of OH^- ion:

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq) \quad K_{sp} = 8.9 \times 10^{-12}$$

The concentration of $Mg^{2+}(aq)$ in sea water is 0.0537 *M*. Will $Mg(OH)_2$ precipitate when enough $Ca(OH)_2$ is added to give a $[OH^-]$ of 0.0010 *M*?

Solution

Calculation of the reaction quotient under these conditions is shown here:

$$Q = \left[Mg^{2+}\right]\left[OH^-\right]^2 = (0.0537)(0.0010)^2 = 5.4 \times 10^{-8}$$

Because *Q* is greater than K_{sp} (\(Q = 5.4 \times 10^{–8}\) is larger than $K_{sp} = 8.9 \times 10^{-12}$), the reverse reaction will proceed, precipitating magnesium hydroxide until the dissolved ion concentrations have been sufficiently lowered, so that $Q_{sp} = K_{sp}$.

Exercise 14.10.7

Predict whether $CaHPO_4$ will precipitate from a solution with $[Ca^{2+}]$ = 0.0001 *M* and = 0.001 *M*.

Answer

No precipitation of $CaHPO_4$; $Q = 1 \times 10^{-7}$, which is less than K_{sp} (7×10^{-7})

Example 14.10.8: Precipitation of AgCl

Does silver chloride precipitate when equal volumes of a 2.0×10^{-4}-M solution of AgNO3 and a 2.0×10^{-4}-M solution of NaCl are mixed?

Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The solubility product is 1.6×10^{-10} (see appendix J).

AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of $AgNO_3$ and NaCl is greater than K_{sp}. Because the volume doubles when equal volumes of $AgNO_3$ and NaCl solutions are mixed, each concentration is reduced to half its initial value

$$\frac{1}{2}\left(2.0 \times 10^{-4}\right) M = 1.0 \times 10^{-4}\ \text{M}$$

The reaction quotient, *Q*, is greater than K_{sp} for AgCl, so a supersaturated solution is formed:

$$Q = \left[Ag^+\right]\left[Cl^-\right] = \left(1.0 \times 10^{-4}\right)\left(1.0 \times 10^{-4}\right) = 1.0 \times 10^{-8} > K_{sp}$$

AgCl will precipitate from the mixture until the dissolution equilibrium is established, with *Q* equal to K_{sp}.

Exercise 14.10.8

Will $KClO_4$ precipitate when 20 mL of a 0.050-*M* solution of K^+ is added to 80 mL of a 0.50-*M* solution of ClO_4^-? (Hint: Use the dilution equation to calculate the concentrations of potassium and perchlorate ions in the mixture.)

Answer

No, $Q = 4.0 \times 10^{-3}$, which is less than $K_{sp} = 1.05 \times 10^{-2}$

Example 14.10.9: Precipitation of Calcium Oxalate

Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion, $C_2O_4^{2-}$, for this purpose (Figure 14.10.4). At sufficiently high concentrations, the calcium and oxalate ions form solid, $CaC_2O_4 \cdot H_2O$ (calcium oxalate monohydrate). The concentration of Ca^{2+} in a sample of blood serum is $2.2 \times 10^{-3} M$. What concentration of $C_2O_4^{2-}$ ion must be established before $CaC_2O_4 \cdot H_2O$ begins to precipitate?



Figure 14.10.4: Anticoagulants can be added to blood that will combine with the Ca^{2+} ions in blood serum and prevent the blood from clotting. (credit: modification of work by Neeta Lind)

Solution

The equilibrium expression is:

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

For this reaction:

$$K_{sp} = \left[Ca^{2+}\right]\left[C_2O_4^{2-}\right] = 1.96 \times 10^{-9}$$

(see Appendix J)

Substitute the provided calcium ion concentration into the solubility product expression and solve for oxalate concentration:

$$\begin{aligned} Q = K_{sp} = \left[Ca^{2+}\right]\left[C_2O_4^{2-}\right] &= 1.96 \times 10^{-9} \\ \left(2.2 \times 10^{-3}\right)\left[C_2O_4{}^{2-}\right] &= 1.96 \times 10^{-9} \\ \left[C_2O_4^{2-}\right] &= \frac{1.96 \times 10^{-9}}{2.2 \times 10^{-3}} \\ &= 8.9 \times 10^{-7}\ \text{M} \end{aligned}$$

A concentration of $\left[C_2O_4^{2-}\right] = 8.9 \times 10^{-7}\ \text{M}$ is necessary to initiate the precipitation of CaC_2O_4 under these conditions.

Exercise 14.10.9

If a solution contains 0.0020 mol of CrO_4^{2-} per liter, what concentration of Ag^+ ion must be reached by adding solid $AgNO_3$ before Ag_2CrO_4 begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

Answer

$6.7\backslash\text{time}10^{-5}\ \text{M}$

Example 14.10.10: Concentrations Following Precipitation

Clothing washed in water that has a manganese $[Mn^{2+}(aq)]$ concentration exceeding 0.1 mg/L (1.8×10^{-6} M) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be decreased by adding a base to precipitate $Mn(OH)_2$. What pH is required to keep $[Mn^{2+}]$ equal to 1.8×10^{-6} M?

Solution

The dissolution of $Mn(OH)_2$ is described by the equation:

$$Mn(OH)_2(s) \rightleftharpoons Mn^{2+}(aq) + 2\,OH^-(aq) \qquad K_{sp} = 2 \times 10^{-13}$$

At equilibrium:

$$K_{sp} = \left[Mn^{2+}\right]\left[OH^-\right]^2$$

or

$$\left(1.8 \times 10^{-6}\right)\left[OH^-\right]^2 = 2 \times 10^{-13}$$

so

$$\left[OH^-\right] = 3.3 \times 10^{-4} M$$

Calculate the pH from the pOH:

$$\begin{aligned} pOH &= -\log\left[OH^-\right] \\ &= -\log(3.3 \times 10^{-4}) = 3.48 \\ pH &= 14.00 - pOH \\ &= 14.00 - 3.48 \\ &= 10.52 \end{aligned}$$

(final result rounded to one significant digit, limited by the certainty of the K_{sp})

Exercise 14.10.10

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of $Ca(OH)_2$. The concentration of $Mg^{2+}(aq)$ in sea water is 5.37×10^{-2} M. Calculate the pH at which $[Mg^{2+}]$ is decreased to 1.0×10^{-5} M

Answer

10.97

In solutions containing two or more ions that may form insoluble compounds with the same counter ion, an experimental strategy called selective precipitation may be used to remove individual ions from solution. By increasing the counter ion concentration in a controlled manner, ions in solution may be precipitated individually, assuming their compound solubilities are adequately different. In solutions with equal concentrations of target ions, the ion forming the least soluble compound will precipitate first (at the lowest concentration of counter ion), with the other ions subsequently precipitating as their compound's solubilities are reached. As an illustration of this technique, the next example exercise describes separation of a two halide ions via precipitation of one as a silver salt.

Chemistry in Everyday Life: The Role of Precipitation in Wastewater Treatment

Solubility equilibria are useful tools in the treatment of wastewater carried out in facilities that may treat the municipal water in your city or town (Figure 14.10.5). Specifically, selective precipitation is used to remove contaminants from wastewater before it is released back into natural bodies of water. For example, phosphate ions are often present in the water discharged from

manufacturing facilities. An abundance of phosphate causes excess algae to grow, which impacts the amount of oxygen available for marine life as well as making water unsuitable for human consumption.



Figure 14.10.5: Wastewater treatment facilities, such as this one, remove contaminants from wastewater before the water is released back into the natural environment. (credit: “eutrophication&hypoxia”/Wikimedia Commons)

One common way to remove phosphates from water is by the addition of calcium hydroxide, or lime, $Ca(OH)_2$. As the water is made more basic, the calcium ions react with phosphate ions to produce hydroxylapatite, $Ca_5(PO4)_3OH$, which then precipitates out of the solution:

$$5\,Ca^{2+} + 3\,PO_4^{3-} + OH^- \rightleftharpoons Ca_5(PO_4)_3 \cdot OH(s)$$

Because the amount of calcium ion added does not result in exceeding the solubility products for other calcium salts, the anions of those salts remain behind in the wastewater. The precipitate is then removed by filtration and the water is brought back to a neutral pH by the addition of CO_2 in a recarbonation process. Other chemicals can also be used for the removal of phosphates by precipitation, including iron(III) chloride and aluminum sulfate.

View this site for more information on how phosphorus is removed from wastewater.

Example 14.10.11: Precipitation of Silver Halides

A solution contains 0.00010 mol of KBr and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgBr or solid AgCl?

Solution

The two equilibria involved are:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = 1.6 \times 10^{-10}$$

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \qquad K_{sp} = 5.0 \times 10^{-13}$$

If the solution contained about *equal* concentrations of Cl^- and Br^-, then the silver salt with the smaller K_{sp} (AgBr) would precipitate first. The concentrations are not equal, however, so the $[Ag^+]$ at which AgCl begins to precipitate and the $[Ag^+]$ at which AgBr begins to precipitate must be calculated. The salt that forms at the lower $[Ag^+]$ precipitates first.

AgBr precipitates when Q equals K_{sp} for AgBr

$$Q_{sp} = K_{sp} = \left[Ag^+\right]\left[Br^-\right] = \left[Ag^+\right](0.00010) = 5.0 \times 10^{-13}$$

$$\left[Ag^+\right] = \frac{5.0 \times 10^{-13}}{0.00010}$$

$$= 5.0 \times 10^{-9}\ M$$

AgBr begins to precipitate when $[Ag^+]$ is $5.0 \times 10^{-9}\ M$.

For AgCl: AgCl precipitates when Q equals K_{sp} for AgCl (1.6×10^{-10}). When $[Cl^-] = 0.10\ M$:

$$Q_{sp} = K_{sp} = \left[\mathrm{Ag^+}\right]\left[\mathrm{Cl^-}\right] = \left[\mathrm{Ag^+}\right](0.10) = 1.6 \times 10^{-10}$$

$$\left[\mathrm{Ag^+}\right] = \frac{1.6 \times 10^{-10}}{0.10}$$

$$= 1.6 \times 10^{-9}\ \mathrm{M}$$

AgCl begins to precipitate when $[Ag^+]$ is 1.6×10^{-9} M.

AgCl begins to precipitate at a lower $[Ag^+]$ than AgBr, so AgCl begins to precipitate first. Note the chloride ion concentration of the initial mixture was significantly greater than the bromide ion concentration, and so silver chloride precipitated first despite having a K_{sp} greater than that of silver bromide.

? Exercise 14.10.11

If silver nitrate solution is added to a solution which is 0.050 *M* in both Cl^- and Br^- ions, at what $[Ag^+]$ would precipitation begin, and what would be the formula of the precipitate?

Answer

$[Ag^+] = 1.0 \times 10^{-11}$ M ; AgBr precipitates first

Common Ion Effect

Compared with pure water, the solubility of an ionic compound is less in aqueous solutions containing a *common ion* (one also produced by dissolution of the ionic compound). This is an example of a phenomenon known as the **common ion effect**, which is a consequence of the law of mass action that may be explained using Le Chatelier's principle. Consider the dissolution of silver iodide:

$$\mathrm{AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)}$$

This solubility equilibrium may be shifted left by the addition of either silver(I) or iodide ions, resulting in the precipitation of AgI and lowered concentrations of dissolved Ag^+ and I^-. In solutions that already contain either of these ions, less AgI may be dissolved than in solutions without these ions.

This effect may also be explained in terms of mass action as represented in the solubility product expression:

$$K_{sp} = \left[\mathrm{Ag^+}\right]\left[\mathrm{I^-}\right]$$

The mathematical product of silver(I) and iodide ion molarities is constant in an equilibrium mixture *regardless of the source of the ions*, and so an increase in one ion's concentration must be balanced by a proportional decrease in the other.

Link to Learning

View this simulation to explore various aspects of the common ion effect.

✓ Example 14.10.12: Common Ion Effect on Solubility

What is the effect on the amount of solid $Mg(OH)_2$ and the concentrations of Mg^{2+} and OH^- when each of the following are added to a saturated solution of $Mg(OH)_2$?

a. $MgCl_2$
b. KOH
c. $NaNO_3$
d. $Mg(OH)_2$

Solution

The solubility equilibrium is

$$\mathrm{Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)}$$

a. Adding a common ion, Mg^{2+}, will increase the concentration of this ion and shift the solubility equilibrium to the left, decreasing the concentration of hydroxide ion and increasing the amount of undissolved magnesium hydroxide.
b. Adding a common ion, OH^-, will increase the concentration of this ion and shift the solubility equilibrium to the left, decreasing the concentration of magnesium ion and increasing the amount of undissolved magnesium hydroxide.
c. The added compound does not contain a common ion, and no effect on the magnesium hydroxide solubility equilibrium is expected.
d. Adding more solid magnesium hydroxide will increase the amount of undissolved compound in the mixture. The solution is already saturated, though, so the concentrations of dissolved magnesium and hydroxide ions will remain the same.

$$Q = \left[Mg^{2+}\right]\left[OH^-\right]^2$$

Thus, changing the amount of solid magnesium hydroxide in the mixture has no effect on the value of Q, and no shift is required to restore Q to the value of the equilibrium constant.

Exercise 14.10.12

What is the effect on the amount of solid $NiCO_3$ and the concentrations of Ni^{2+} and CO_3^{2-} when each of the following are added to a saturated solution of $NiCO_3$

a. $Ni(NO_3)_2$
b. $KClO_4$
c. $NiCO_3$
d. K_2CO_3

Answer

(a) mass of $NiCO_3(s)$ increases, $[Ni^{2+}]$ increases, CO_3^{2-} decreases; (b) no appreciable effect; (c) no effect except to increase the amount of solid $NiCO_3$; (d) mass of $NiCO_3(s)$ increases, $[Ni^{2+}]$ decreases, CO_3^{2-} increases;

Example 14.10.13: Common Ion Effect

Calculate the molar solubility of cadmium sulfide (CdS) in a 0.010-*M* solution of cadmium bromide ($CdBr_2$). The K_{sp} of CdS is 1.0×10^{-28}.

Solution

This calculation can be performed using the ICE approach:

$$CdS(s) \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq)$$

	$CdS(s) \rightleftharpoons Cd^{2+}(aq)$	+ $S^{2-}(aq)$	
Initial concentration (*M*)		0.010	0
Change (*M*)		$+x$	$+x$
Equilibrium concentration (*M*)		$0.010 + x$	x

$$K_{sp} = \left[Cd^{2+}\right]\left[S^{2-}\right] = 1.0 \times 10^{-28}$$
$$(0.010 + x)(x) = 1.0 \times 10^{-28}$$

Because Ksp is very small, assume $x \ll 0.010$ and solve the simplified equation for x:

$$(0.010)(x) = 1.0 \times 10^{-28}$$
$$x = 1.0 \times 10^{-26}\ \text{M}$$

The molar solubility of CdS in this solution is $1.0 \times 10^{-26}\ \text{M}$.

Exercise 14.10.13

Calculate the molar solubility of aluminum hydroxide, $Al(OH)_3$, in a 0.015-*M* solution of aluminum nitrate, $Al(NO_3)_3$. The K_{sp} of $Al(OH)_3$ is 2×10^{-32}.

Answer

$4 \times 10^{-11}\ \text{M}$

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14.E: Acid-Base Equilibria (Exercises)

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

Q3

Vinegar contains acetic acid CH_3COOH. What species serves as a base when vinegar is mixed with baking soda, sodium bicarbonate, during the preparation of bread?

Solution

$$NaHCO_3 + CH_3COOH \rightarrow NaCH_3COO + CO_2 + H_2O$$

$NaHCO_3$ serves as the base.

Q7

a. Thinking of acid-base reaction in terms of oxide donors and oxide acceptors, is the base oxide donors or oxide acceptors?
b. Identify the acid and base in the reaction:

$$CaO + CO_2 \rightleftharpoons CaCO_3$$

Solution

a. The base is the oxide donor. We can distinctly see this in the autoionization of H_2O, where OH^- counts as the basic part
b. CaO is the base, and CO_2 is the acid.

Q5

Baking soda known as $NaHCO_3$ is formed by adding water and carbon dioxide to sodium carbonate.

a. Write a balanced equation for this chemical reaction
b. Is this a Brønsted-Lowry acid-base reaction? What is a Brønsted-Lowry acid? What is a Brønsted-Lowry base?

Solution

a. $Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$
b. This is not a Brønsted-Lowry acid-base reaction because it does not involve a transfer of an H^+ ion. A Brønsted-Lowry acid is a proton donor, and a Brønsted-Lowry base is a proton acceptor.

Q9

Identify each of the following oxides as an acid or base anhydride:

a. CaO
b. P_2O_5

Solution

a. CaO is the base anhydride of calcium hydroxide $Ca(OH)_2$.
b. P_2O_5 is the acid anhydride of phosphoric acid H_3PO_4.

Q11

Al(III) oxide is amphoteric. What is the balanced chemical equation of Al(III) oxide react with aqueous H_2SO_4? What is the balanced equation of it reacts with KOH?

Solution

$$Al_2O_3(s) + 3\,H_2SO_4(aq) \rightleftharpoons Al_2(SO_4)_3(aq) + 3\,H_2O(l)$$

\ce{Al2O3 + 2KOH + 3H2O \rightleftharpoons 2KAl(OH)4 \nonumber

Q13

The $[H_3O^+]$ concentration in a glass of orange juice is 3.96 x 10^{-5} M. What is the juice's pH?

Solution

$$pH = -\log[H_3O+]$$

Since the concentration of hydronium ions is given, the pH calculation is as follows:

$$pH = -\log[3.96 \times 10^{-5}] = 4.4023$$

pH is a measure of hydrogen ions in a solution. This concentration defines the acidity or alkalinity of a solution.

Q17

The pK_w of an unknown salty water at 25 °C is 13.665. This differs from the usual K_w of 14.00 at this temperature because dissolved salts make this unknown salty water a non- ideal solution. If the pH in the salty water is 7.8, what are the concentrations of H_3O^+ and OH^- in the salty water at 25 °C?

Solution

$\mathrm{pH} = -\log[\mathrm{H_3O^+}]$, hence,

$[\mathrm{H_3O^+}] = 10^{-7.8} = 1.5849 \times 10^{-}8\ \mathrm{M}$

Since $\mathrm{pK_w} = [\mathrm{OH^-}][\mathrm{H_3O^+}]$,

$[\mathrm{OH^-}] = \frac{10^{-13.665}}{1.5849 \times 10^{-8}\ \mathrm{M}} = 1.3645 \times 10^{-6}\mathrm{M}$

Q19

When rubidium (Rb) solid is added to water, there is an instantaneous and vigorous reaction (i.e., an explosion) as this video demonstrates. Based on this information, which of these two equations is a more accurate representation the reaction?

$$2\,\mathrm{Rb(s)} + 2\,\mathrm{H_2O(l)} \rightarrow 2\,\mathrm{RbOH(aq)} + \mathrm{H_2(aq)}$$

$$2\,\mathrm{Rb(s)} + 2\,\mathrm{H_3O^+(aq)} \rightarrow 2\,\mathrm{Rb^+(aq)} + \mathrm{H_2(aq)} + 2\,\mathrm{H_2O(l)}$$

Solution

The equation:

$$2\,\mathrm{Rb(s)} + 2\,\mathrm{H_2O(l)} \rightarrow 2\,\mathrm{RbOH(aq)} + \mathrm{H_2(aq)}$$

Is a better representation of Rb being placed into water. It represents the direct interaction between the alkali metal and water. We know from the problem that the reaction is fast, vigorous, and forceful. The second equation represents a reaction in equilibrium, one that we would expect to be slow as there are only 1x10^{-7}mol/L of H_3O^+ in a 1L of water. Even if the reaction were vigorous at the low concentration of hydronium ions, there would not be enough of them to keep up with the speed of the reaction (they would become a limiting reactant), hence slowing or stopping the reaction from proceeding.

Q23

In the following chemical equation determine which species is the strongest acid and which is the strongest base, using the Brønsted–Lowry definition. At equilibrium, is there a greater concentration of reactants or products present?

a. $$\mathrm{HIO_{3\ (aq)} + HCOO^-_{(aq)} \rightleftharpoons HCOOH_{(aq)} + IO^-_{3\ (aq)}}$$

b. $$\left(\mathrm{HIO_{3\ (aq)} \rightleftharpoons IO^-_{3\ (aq)}} \qquad \mathrm{K_a = 1 \cdot 6 \times 10^{-1}}\right)$$

c. $$\left(\mathrm{HCOOH_{(aq)} \rightleftharpoons HCOO^-_{(aq)}} \qquad \mathrm{K_a = 1 \cdot 8 \times 10^{-4}}\right)$$

Solution

A Brønsted–Lowry acid is the species that donates protons in a solution. When comparing two different weak acids in solution, like:

$$\mathrm{HIO_{3\ (aq)} + HCOO^-_{(aq)} \rightleftharpoons HCOOH_{(aq)} + IO^-_{3\ (aq)}}$$

We can compare their abilities to donate protons to see which one is the stronger of the two weak acids.

$$\mathrm{HIO_{3\ (aq)} + H_2O_{(aq)} \rightleftharpoons IO^-_{3\ (aq)} + H_3O^+_{(aq)} \qquad K_a = 1 \cdot 6 \times 10^{-1}}$$

$$\mathrm{HCOOH_{(aq)} + H_2O_{(aq)} \rightleftharpoons HCOO^-_{(aq)} + H_3O^+_{(aq)} \qquad K_a = 1 \cdot 8 \times 10^{-4}}$$

Seeing that $\mathrm{K_a = 1 \cdot 6 \times 10^{-1} > K_a = 1 \cdot 8 \times 10^{-4}}$, we know $\mathrm{HIO_3}$ is the stronger acid.

A Brønsted–Lowry base is the species that accepts protons. So in this case, we must examine which of the two weak acids has a stronger conjugate base, which means we must find the $\mathrm{K_b}$ for the reactions of the conjugate bases.

We know that:

$$\mathrm{K_w = K_a \times K_b}$$

and

$$\mathrm{K_w = 1.0 \times 10^{-7}}$$

So we can find $\mathrm{K_b}$ by dividing $\mathrm{K_w}$ by $\mathrm{K_a}$ which ultimately gives us:

$$\mathrm{IO^-_{3\ (aq)} + H_2O_{(aq)} \rightleftharpoons HIO_{3\ (aq)} + OH^-_{(aq)} \qquad K_b = 6 \cdot 3 \times 10^{-14}}$$

$$\mathrm{HCOO^-_{(aq)} + H_2O_{(aq)} \rightleftharpoons HCOOH_{(aq)} + OH^-_{(aq)} \qquad K_b = 5 \cdot 6 \times 10^{-11}}$$

Seeing that $\mathrm{K_b = 5 \cdot 6 \times 10^{-11} > K_a = 6 \cdot 3 \times 10^{-14}}$, we know $\mathrm{HCOO^-}$ is the stronger base.

To determine whether there is a greater concentration of reactants or products present, the K value for the overall reaction must be determined. The overall reaction is the product of the first given reaction and the reverse of the second given reaction. Dividing the first value for $\mathrm{K_a}$ by the second gives

$$K = 888$$

$$K > 1$$

which indicates that at equilibrium, there is a greater concentration of products than reactants.

Q27

Acetic acid gives vinegar a sour taste and strong aroma. Its K_a value is 1.75 x 10^{-5}. What is the pH of the solution if 0.59 grams of acetic acid is dissolved in 40 mL of water?

Solution

First, convert grams of acetic acid to moles.

$$(0.59\ g\ CH_3COOH)\left(\frac{1\ mol}{60.05\ g\ CH_3COOH}\right) = 0.0098\ mol$$

Then, find the molarity of acetic acid by dividing the number of moles of acetic acid by the number of liters of water.

$$\frac{0.0098\ mol}{0.04\ L\ water} = 0.246\ M$$

Using the molarity and $\mathrm{K_a}$, construct and solve an ICE table to find out how much the acetic acid dissociates.

$\mathrm{CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}}$

	CH_3COOH	H_2O	CH_3COO^-	H_3O^+

I	0.246	---	0	0
C	-x	---	+x	+x
E	0.246-x	---	x	x

The acid dissociation constant works in the below equation:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Plug in the final concentration values from the ICE table and solve for x.

$$1.75 \times 10^{-5} = \frac{x^2}{0.246 - x}$$

$$x = 0.0021$$

Use the calculated value of x to calculate the concentration of H_3O+, which in this case is equal to x. Then, plug this concentration into the equation for pH.

$$pH = -log[0.0021]$$

$$pH = 2.6848$$

Q29

a. A student prepares a solution of 0.60M of formic acid carefully in a water bath that remains constant at 25°C, determine the pH of the solution. (Ka of formic acid: 1.8 x 10^{-4})
b. How many grams of trichloroacetic acid should be dissolved per liter of deionized water so that the solution of trichloroacetic acid would have the same pH as that of the formic acid solution in a)? (Ka of trichloroacetic acid is 2.2 x 10^{-1})

Solution

Construct an ICE table based on the equation:

$$\mathrm{HCOOH + H_2O \rightleftharpoons HCO_2^- + H_3O^+}$$

	$HCOOH$	H_2O	HCO_2^-	H_3O^+
I	0.6	-	0	0
C	-x	-	+x	+x
E	0.6-x	-	x	x

Ka can then be equated to an algebraic expression:

$$\mathrm{Ka} = \frac{\mathrm{x}^2}{0.6 - \mathrm{x}}$$

$$1.8 \times 10^{-4} = \frac{\mathrm{x}^2}{0.6 - \mathrm{x}}$$

$$\mathrm{x} = 0.0103026$$

or

$$\mathrm{x} = -0.0104$$

x must be postive. Thus, x = 0.0103026.

$$[H_3O^+]$$

$$pH = -\log(0.0103026) = 1.987$$

Because we know the pH we want to attain (1.987), we have start by first finding $[H_3O^+]$:

$$-\log[H_3O^+] = 1.987$$

$$[H_3O^+] = 10^{-1.987}$$

$$[H_3O^+] = 0.0103026$$

An ICE table can also be constructed for the reaction:

$$CCl_3CO_2H + H_2O \rightleftharpoons CCl_3CO_2^- + H_3O^+$$

	CCl_3CO_2H	H_2O	$CCl_3CO_2^-$	H_3O^+
I	x	-	0	0
C	-0.010303	-	+0.010303	+0.010303
E	x-0.010303	-	0.010303	0.010303

$$K_a = \frac{(0.010303)^2}{(x - 0.010303)}$$

$$2.2 \times 10^{-1} = \frac{(0.010303)^2}{(x - 0.010303)}$$

$$x = 0.0107855 M$$

To calculate the mass of trichloroacetic acid, we can calculate the molarity of trichloroacetic acid by its molar mass.

$$\text{Mass of trichloroacetic acid} = 0.0107855 \text{ M} \times (35.5 \frac{g}{mol} \times 3 + 12 \frac{g}{mol} \times 2 + 16 \frac{g}{mol} \times 2 + 1 \frac{g}{mol}) = 1.76 \text{ g}$$

Q41

Rank each of the 0.2 M solution below in an order of increasing pH: NH_4I, KF, HCl, KCl, KOH.

Solution

$$HCl < NH_4I < KF < KCl < KOH$$

Q43

0.040 mol of Diethylamine ($C_4H_{11}N$, pK_b =11.09) is titrated with 0.015 mol of HCl in a 1.00L wash bottle, calculate the pH value of the solution.

Solution

Because equivalence point is not reached yet, we can employ Henderson-Hasselbalch equation.

$$pOH \approx pK_b + \log \frac{[BH^+]}{[B]}$$

$$pOH \approx (11.09) + \log \frac{[C_4H_{12}N^+]}{[C_4H_{11}N]}$$

$$pOH \approx (11.09) + \log \frac{0.015}{0.040 - 15}$$

$$pOH \approx 10.87$$

At room temperature $K_w = 14$ and

$$\begin{aligned} pH &= pK_w - pOH \\ &= 14.00 - 10.87 \\ &= 3.13 \end{aligned}$$

Q45

Prepare a Hypochlorous acid/Hypochlorite buffer at pH 7.

a. Suppose you only have 0.5 mol of lithium hypochlorite, but an infinite supply of hypochlorous acid (pKa = 7.53) and water. How many moles of hypochlorous acid should you use, assuming you use all 0.5 mol of lithium hypochlorite, and dilute the buffer to 100 mL?
b. Suppose Professor Güntherfœrd's arm was doused in about 0.12 moles total HCl. Will this buffer be enough to bring her arm up to a pH over 6.5?

Solution

Using the Henderson–Hasselbalch approximation:

$$\mathrm{pH} \approx \mathrm{pK_a} + \log \frac{[\mathrm{ClO^-}]_o}{[\mathrm{HClO}]_o}$$

It's easy to re-arrange the equation to solve for $[\mathrm{HClO}]_\circ$. Multiplying by 100 mL yields the moles of acid added.

$$\mathrm{pH} \approx \mathrm{pK_a} + \log \frac{[\mathrm{ClO^-}]_o}{[\mathrm{HClO}]_o}$$

$$7 \approx \mathrm{pK_a} + \log \frac{[\mathrm{ClO^-}]_o}{[\mathrm{HClO}]_o}$$

$$7 \approx 7.53 + \log \frac{5}{[\mathrm{HClO}]_o}$$

$$[\mathrm{HClO}]_\circ \approx 16.94$$

$$\text{Moles HClO} \approx 1.694$$

Q49

A student is given 500 mL of a 0.500 M acetic acid solution and wants to create a pH 5.0 buffer. How many mL of 1 M NaOH must be added to the original solution? Acetic acid has a $\mathrm{pK_a}$ of 4.756.

Solution

We first use the Henderson-Hasselbach approximation to determine the required ratio of base to acid in the solution:

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$

$$5.00 = 4.756 + \log\left(\frac{[base]}{[acid]}\right)$$

$$0.244 = \log\left(\frac{[base]}{[acid]}\right)$$

$$1.75 = \frac{[base]}{[acid]}$$

Next, we will determine the molar amount of base required to get a pH of 5.00. In order to simplify things we will first solve for the molar quantities as of each using the simple ratio above in relation to 1.75:

$$\text{Acetic Acid in 500 mL solution} = (0.5\ M) \times (0.5\ L)$$

$$= 0.25\ mol$$

$$NaOH\ in\ 500\ mL\ solution = (0.25\ mol) \times (1.75) + 0.25 = 0.6875 +\ mol$$

Now we'll determine the volume of 1M NaOH needed to raise the pH:

$$\left(\frac{1\ mol}{1\ L}\right) = \left(\frac{0.6875\ mol}{x}\right)$$

$$s = 0.6875\ L\ NaOH$$

Now we'll check to make sure everything is right:

$$Acetic\ Acid\ = \left(\frac{0.25}{0.9375}\right) = 0.2667M$$

$$NaOH\ = \left(\frac{0.6875 - 0.25}{0.9375}\right) = 0.4667M$$

$$5.00 = 4.756 + \log\left(\frac{[base]}{[acid]}\right)$$

$$pH = 4.756 + \log\left(\frac{[0.4667]}{[0.2667]}\right)$$

$$pH = 4.756 + 0.243 = 4.999$$

We get a pH of 4.999 which is about 5.00 and isn't exactly 5.00 due to rounding early in the problem, so the problem was done correctly.

Q51

0.15M of HBr is added into 50mL of 0.1M $Ca(OH)_2$ for the titration.

a. What is the pH of the solution before HBr is added?
b. What is the pH of the solution at the point when it needs 1 mL of HBr to neutralize the solution?
c. What is the pH of the solution when it is titrated 1 mL past neutralization?

Solution

$$2HBr + Ca(OH)_2 \rightleftharpoons 2H_2O + CaBr_2 \tag{14.E.1}$$

a) $Ca(OH)_2$ is strong base. They dissociate completely.

$$[\mathrm{OH^-}] = 2[\mathrm{Ca(OH)_2}] = 0.2\mathrm{M}$$

$$\mathrm{pH} = \mathrm{pK_w} - \mathrm{pOH}$$

$$\mathrm{pH} = 14 + \log(0.2\ \mathrm{M})$$

$$\mathrm{pH} = 13.3$$

b) Because $Ca(OH)_2$ and HBr are both strong base and strong acid, at equilibrium, the pH is 7.00.

$$\mathrm{mole}_{\mathrm{Ca(OH)_2}} = (\mathrm{Volume})(\mathrm{Molarity}) \tag{14.E.2}$$

$$\mathrm{mole}_{\mathrm{Ca(OH)_2}} = (0.05\mathrm{L})(0.1\mathrm{M}) \tag{14.E.3}$$

$$\mathrm{mole}_{\mathrm{Ca(OH)_2}} = 0.005\ \mathrm{mol} \tag{14.E.4}$$

@ equilibrium;

$$\mathrm{mole}_{\mathrm{HBr}} = 2\ \mathrm{mole}_{\mathrm{Ca(OH)_2}} \tag{14.E.5}$$

$$\mathrm{mole}_{\mathrm{HBr}} = 2(0.005\ \mathrm{mol}) = 0.01\ \mathrm{mol} \tag{14.E.6}$$

$$\mathrm{Volume}_{\mathrm{HBr}} = \frac{\mathrm{mole}_{\mathrm{HBr}}}{\mathrm{molarity}_{\mathrm{HBr}}} = \frac{0.01\ \mathrm{mol}}{0.15\mathrm{M}} = 0.0667\ \mathrm{L} = 66.7\ \mathrm{mL} \tag{14.E.7}$$

$$\mathrm{Total\ Volume\ at\ equilibrium} = 66.7\mathrm{mL} + 50\mathrm{mL} = 116.7\mathrm{mL} \tag{14.E.8}$$

$$\mathrm{Total\ Volume\ 1mL\ short\ of\ equilibrium} = 116.7\mathrm{mL} - 1\mathrm{mL} = 115.7\mathrm{mL} \tag{14.E.9}$$

$$\mathrm{Volume}_{\mathrm{HBr}}\ 1\mathrm{mL\ short\ of\ equilibrium} = 66.7\mathrm{mL} - 1\mathrm{mL} = 65.7\ \mathrm{mL} \tag{14.E.10}$$

$$\mathrm{mols\ of\ OH^-\ not\ neutralized\ by\ HBr} = 0.01\ \mathrm{mol} - 0.0657\ \mathrm{L} \times (0.15\ \mathrm{M}) = 1.45 \times 10^{-4}\ \mathrm{mol} \tag{14.E.11}$$

$$\mathrm{pH} = 14 + \log\left(\frac{1.45^{-4}\ \mathrm{mol}}{0.1157\ \mathrm{L}}\right) = 11.1 \tag{14.E.12}$$

c)

At 1mL after equilibrium, $Ca(OH)_2$ has been neutralized by HBr. Only HBr exists in the solution.

$$\mathrm{mole}_{\mathrm{HBr}} = (0.001\mathrm{L})(0.15\mathrm{M}) = 1.5 \times 10^{-4}\ \mathrm{mol} \tag{14.E.13}$$

$$\mathrm{Volume} = \mathrm{Total\ Volume} + 1\mathrm{mL} = 117.7\mathrm{mL} = 0.1177\ \mathrm{L} \tag{14.E.14}$$

$$\mathrm{M}_{\mathrm{HBr}}\ \mathrm{in\ the\ solution} = \frac{1.5 \times 10^{-4}\ \mathrm{mol}}{0.1177\ \mathrm{L}} = 1.274 \times 10^{-3}\mathrm{M} \tag{14.E.15}$$

$$\mathrm{M}_{\mathrm{HBr}}\ \mathrm{in\ the\ solution} = \mathrm{M}_{\mathrm{H^+}}\ \mathrm{in\ the\ solution} \tag{14.E.16}$$

$$\mathrm{pH} = -\log[\mathrm{H^+}] = -\log(1.274 \times 10^{-3}\mathrm{M}) = 2.89 \tag{14.E.17}$$

Q55

K_b at 25°C for Diethylamine ($(C_2H_5)_2NH$) is 1.3×10^{-3}. Consider the titration of 50.00 mL of a 0.1000 M solution of Diethylamine with 0.100 M HCl added with the following volumes: 0, 10.00, 50.00 mL. Calculate pH for each solutions. At an unknown volume beyond 50.00 mL, the pH is 3.90. Find the corresponding amount volume of HCl needed to obtain that pH.

Solution

When HCl volume = 0.00 mL.

$$DiEtNH_{(aq)} + H_2O_{(l)} \rightleftharpoons DiEtNH^+_{2(aq)} + OH^-_{aq} \tag{14.E.18}$$

$$\frac{[DiEtNH_2^+][OH^-]}{[DiEtNH]} = 1.3 \times 10^{-3} \tag{14.E.19}$$

$$[OH^-] = [DiEtNH_2^+] = y$$

$$[DiEtNH] = 0.1000 - y$$

$$\frac{y^2}{0.1000-y}=1.3\times10^{-3} \tag{14.E.20}$$

$$\mathrm{y}=0.01077\mathrm{M}=[\mathrm{OH}^-]$$

$$\mathrm{pOH}=1.97$$

$$\mathrm{pH}=12.03$$

When HCl volume = 10.00 mL.

$$[\mathrm{DiEtNH}_2^+]=\frac{(0.1000\mathrm{M})(0.01\mathrm{L})}{(0.050+0.010)\mathrm{L}}=0.0167\ \mathrm{M} \tag{14.E.21}$$

$$[\mathrm{DiEtNH}]=\frac{(0.1000\mathrm{M}(0.050\mathrm{L})-(0.1000\mathrm{M})(0.01\mathrm{L})}{(0.050+0.010)\mathrm{L}}=0.0667\ \mathrm{M} \tag{14.E.22}$$

Plug it back to Henerson Hasselbalch equation

$$\mathrm{pOH}=\mathrm{pK_b}+\log(\frac{[\mathrm{BH}^+]}{[\mathrm{B}]}) \tag{14.E.23}$$

\[\mathrm{pOH = -\log(1.3 \times 10^{-3}) +\log(\dfrac{[0.0167 \; M]}{[0.0667 \; M]})}$$

$$\mathrm{pH}=\mathrm{pH}-\mathrm{pOH}=14.00-2.28=11.72 \tag{14.E.24}$$

When HCl volume = 50 mL.

The titration is at the equivalence point. At equivalence, the reaction consists of 100 mL of 0.050 mol DiEtNH_2^+

$$\mathrm{DiEtNH}_{2(\mathrm{aq})}^+ + \mathrm{H_2O}_{(\mathrm{l})} \rightleftharpoons \mathrm{DiEtNH}_{(\mathrm{aq})} + \mathrm{H_3O}_{(\mathrm{aq})}^+ \tag{14.E.25}$$

$$\mathrm{K_a}=\frac{1.00\times10^{-14}}{1.3\times10^{-3}}=7.69\times10^{-12}$$

$$\mathrm{K_a}=7.69\times10^{-12}=\frac{\mathrm{x}^2}{(0.5000-\mathrm{x})};\mathrm{x}=[\mathrm{H_3O}^+] \tag{14.E.26}$$

$$\mathrm{x}=1.96\times10^{-6};\mathrm{pH}=5.71$$

Beyond the equivalence point

Beyond the equivalence point, solution behaves like HCl.

Given pH = 3.90.

$$10^{-3.90}=\frac{(\mathrm{z}-0.050\ \mathrm{L})}{0.100\ \mathrm{L}+\mathrm{z}}\times0.1000\ \mathrm{M} \tag{14.E.27}$$

$\mathrm{z}=0.0502\ \mathrm{L}$

Q57

Sodium Bicarbonate ($\mathrm{NaHCO_3}$) is a very weak base when dissolved in water. Some amount of sodium bicarbonate is dissolved in 125 mL of a 0.25 M solution of $\mathrm{HNO_3}$. The 168 mL of 0.15 M NaOH was used to titrate the solution. How many grams of sodium bicarbonate were added?

Solution

We are titrating an acid with two bases so solve for the amount of acid the NaOH neutralizes and the remaining moles of acid will be the number of moles of sodium bicarbonate.

$$\mathrm{Moles\ HNO_3}=\frac{0.25\ \mathrm{moles}}{1\ \mathrm{L}}\times0.125\ \mathrm{L}=0.03125\ \mathrm{moles}$$

$$\text{Moles NaOH} = \frac{0.15 \text{ moles}}{1 \text{ L}} \times 0.168 \text{ L} = 0.0252 \text{ moles}$$

$$0.03125 - 0.0252 = 0.00605 \text{ moles sodium bicarbonate}$$

Now just multiply by sodium bicarbonate's molar mass (84.007 $\frac{g}{mol}$) to find the mass of sodium bicarbonate added

$$0.00605 \times 84.007 = 0.51\text{g}$$

Q59

What is the molarity of a HNO_3 water solution if it requires 31.80 mL of such solution to titrate 0.0662 g Aniline in 100 mL aqueous solution to equivalence point? What will the pH value be at the equivalence point if $\text{K}_\text{b}(\text{Aniline}) = 3.8 \times 10^{-10}$?

Solution

Aniline and HNO_3 react with a one-to-one stoichiometry

$$\text{C}_6\text{H}_5\text{NH}_2(\text{aq}) + \text{HNO}_3(\text{aq}) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+(\text{aq}) + \text{NO}_3^-(\text{aq})$$

Therefore

$$M(HNO_3) = \frac{0.0662\ g}{93.13\ g/mol} \times \frac{1}{0.03180\ L} = 0.0224\ M$$

Suppose at the equivalence point all Aniline is converted to its conjugate acid, then its concentration equals

$$[\text{C}_6\text{H}_5\text{NH}_3^+] = \frac{0.0662\,g}{(93.13\,g/mol)\ 0.1318\,L} = 0.00539\,M$$

Also as some Aniline's conjugate acid reacts with water,

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{3.8 \times 10^{-10}} = 2.63 \times 10^{-5} = \frac{[H_3O^+][C_6H_5NH_2]}{[C_6H_5NH_3^+]} = \frac{x^2}{0.00539 - x}$$

Therefore,

$$x = [H_3O^+] = 3.636 \times 10^{-4} M$$

so $\text{pH} = 3.44$.

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CHAPTER OVERVIEW

15: Thermodynamics

Among the many capabilities of chemistry is its ability to predict if a process will occur under specified conditions. Thermodynamics, the study of relationships between the energy and work associated with chemical and physical processes, provides this predictive ability. Previous chapters in this text have described various applications of thermochemistry, an important aspect of thermodynamics concerned with the heat flow accompanying chemical reactions and phase transitions. This chapter will introduce additional thermodynamic concepts, including those that enable the prediction of any chemical or physical changes under a given set of conditions.

15.1: Introduction
15.2: Spontaneity
15.3: Entropy
15.4: The Second and Third Laws of Thermodynamics
15.5: Free Energy
15.6: Key Terms
15.7: Key Equations
15.8: Summary
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15.1: Introduction

Among the many capabilities of chemistry is its ability to predict if a process will occur under specified conditions. Thermodynamics, the study of relationships between the energy and work associated with chemical and physical processes, provides this predictive ability. Previous chapters in this text have described various applications of thermochemistry, an important aspect of thermodynamics concerned with the heat flow accompanying chemical reactions and phase transitions. This chapter will introduce additional thermodynamic concepts, including those that enable the prediction of any chemical or physical changes under a given set of conditions.



Figure 15.1.1: Geysers are a dramatic display of thermodynamic principles in nature. Water deep within the underground channels of the geyser is under high pressure and heated to high temperature by magma. When a pocket of water near the surface reaches boiling point and is expelled, the resulting drop in pressure causes larger volumes of water to flash boil, forcefully ejecting steam and water in an impressive eruption. (credit: modification of work by Yellowstone National Park)

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15.2: Spontaneity

Learning Objectives

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

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. Iron exposed to the earth's atmosphere will corrode, but rust is not converted to iron without intentional chemical treatment. A **spontaneous process** is one that occurs naturally under certain conditions. A **nonspontaneous process**, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure 15.2.1).

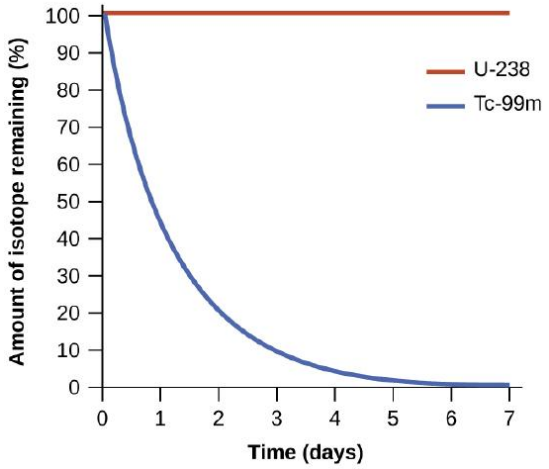


Figure 15.2.1: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.

As another example, consider the conversion of diamond into graphite (Figure 15.2.2).

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

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow; so, for all practical purposes diamonds are indeed "forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

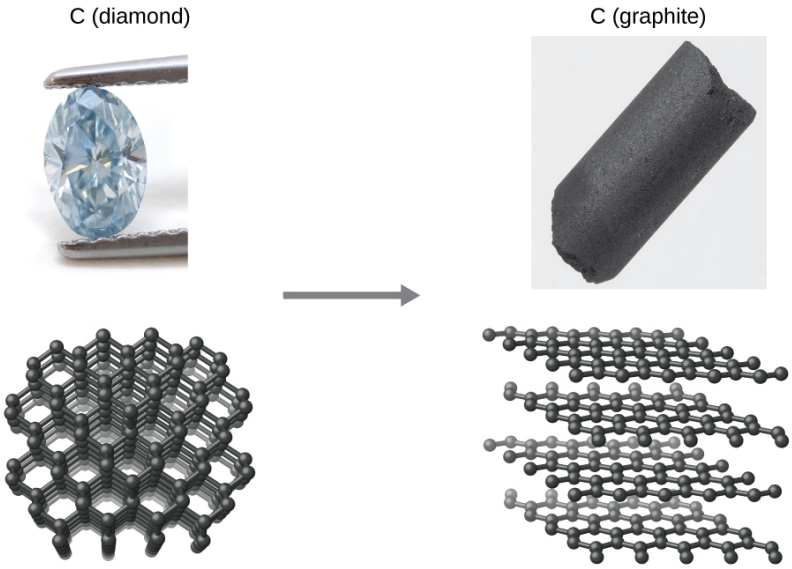


Figure 15.2.2: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as *graphitization*, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

Dispersal of Matter and Energy

Extending the discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas in one flask and the other flask is empty ($P = 0$) (Figure 15.2.3). When the valve is opened, the gas spontaneously expands to fill both flasks equally. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

\[w=-P \Delta V=0 \quad \quad (P=0 \text { in a vacuum })|]

Note as well that since the system is isolated, no heat has been exchanged with the surroundings (q = 0). The *first law of thermodynamics* confirms that there has been no change in the system's internal energy as a result of this process.

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

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the driving force appears to be related to the *greater, more uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous expansion took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

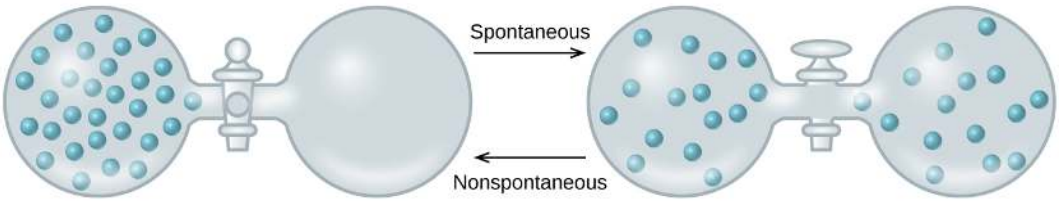


Figure 15.2.3: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure 15.2.4). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

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

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.



Figure 15.2.4: When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

Example 15.2.1: Redistribution of Matter during a Spontaneous Process

Describe how matter is redistributed when the following spontaneous processes take place:

a. A solid sublimes.
b. A gas condenses.
c. A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution



Figure 15.2.5: (credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Paul A. Flowers)

a. Sublimation is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition.
b. Condensation is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition.
c. The process in question is diffusion. This process yields a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop of dye, zero in the water), and the final state of the system contains a single dye concentration throughout.

Exercise 15.2.1

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

Answer

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

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15.3: Entropy

Learning Objectives

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

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

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure 15.3.1) published the results of an extensive study regarding the efficiency of steam heat engines. A later review of Carnot's findings by Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). In thermodynamics, a **reversible process** is one that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change in some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.

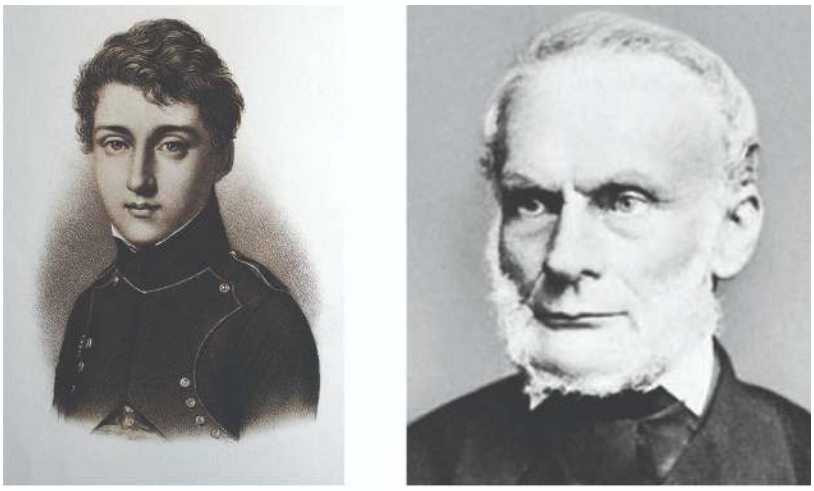


Figure 15.3.1: (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property entropy (S) and defined its change for any process as the following:

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

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

Entropy and Microstates

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

$$S = k \ln W$$

where k is the Boltzmann constant, 1.38 10^{-23} J/K.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

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

For processes involving an increase in the number of microstates, $W_f > W_i$, the entropy of the system increases and $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $W_f < W_i$, yield a decrease in system entropy, $\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

Consider the general case of a system comprised of N particles distributed among n boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in $2^4 = 16$ different microstates as illustrated in Figure 15.3.2 Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

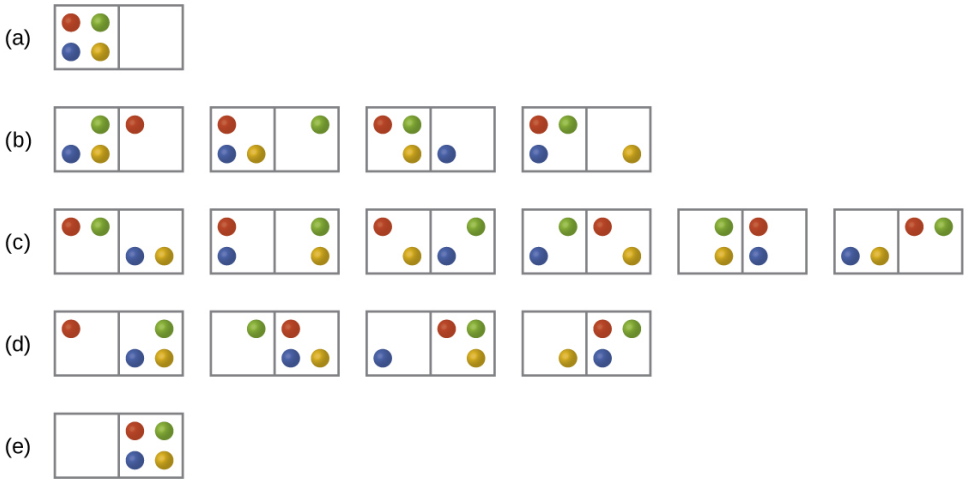


Figure 15.3.2: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

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

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

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

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

The previous description of an ideal gas expanding into a vacuum (Figure 16.4) is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. Initially, the gas molecules are confined to just one of the two flasks. Opening the valve between the flasks increases the volume available to the gas molecules and, correspondingly, the number of microstates possible for the system. Since $W_f > W_i$, the expansion process involves an increase in entropy ($\Delta S > 0$) and is spontaneous.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of thermal energy (represented as "*") in Figure 15.3.3 The hot object is comprised of

particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. Thus, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects' temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

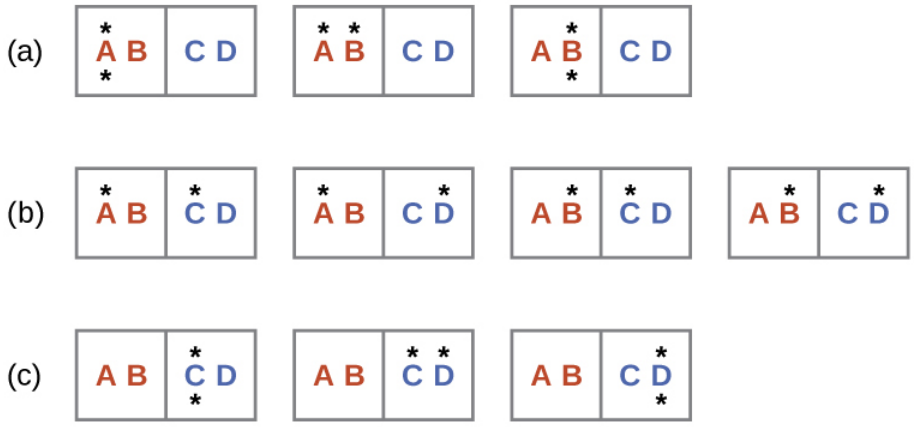
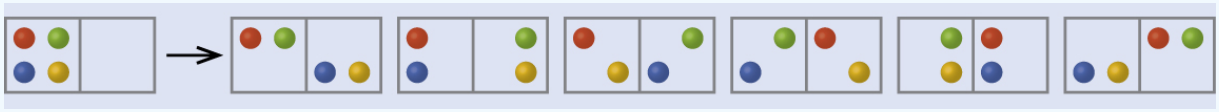


Figure 15.3.3: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

Example 15.3.1: Determination of ΔS

Calculate the change in entropy for the process depicted below.



Solution

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

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

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

Exercise 15.3.1

Consider the system shown in Figure 15.3.3. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer

0 J/K

Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure 15.3.4 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, $\Delta S < 0$.

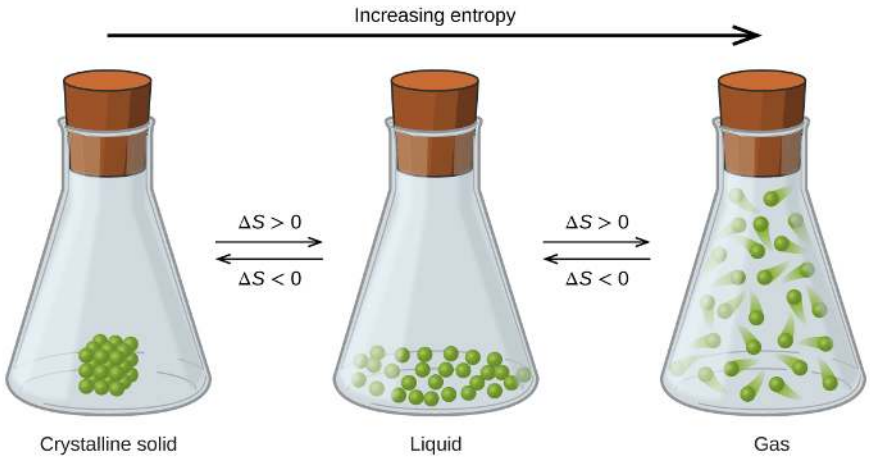


Figure 15.3.4: The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the gaseous phase, in which a given number of atoms or molecules occupy a *much* greater volume than in the liquid phase. Each atom or molecule can be found in many more locations, corresponding to a much greater number of microstates. Consequently, for any substance, $S_{gas} > S_{liquid} > S_{solid}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure 15.3.5).

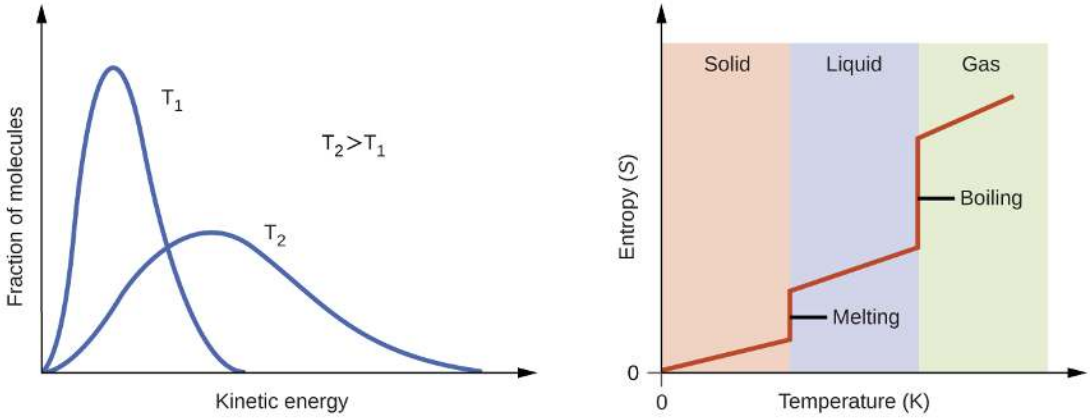


Figure 15.3.5: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance undergoes a phase transition, its entropy changes significantly.

Link to Learning

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

The entropy of a substance is influenced by the structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (a topic beyond the scope of this text). For molecules, greater numbers of atoms increase the number of ways in which the molecules can vibrate and thus the number of possible microstates and the entropy of the system.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in Example 15.3.2

Example 15.3.2: Predicting the Sign of ΔS

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

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

Solution

a. positive, temperature increases
b. negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter
c. negative, net decrease in the amount of gaseous species
d. positive, phase transition from solid to liquid, net increase in dispersal of matter

Exercise 15.3.1

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

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

Answer

(a) Positive; The solid dissolves to give an increase of mobile ions in solution.

(b) Negative; The liquid becomes a more ordered solid.

(c) Positive; The relatively ordered solid becomes a gas.

(d) Positive; There is a net increase in the amount of gaseous species.

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15.4: The Second and Third Laws of Thermodynamics

Learning Objectives

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

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

The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, a promising candidate has been identified: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

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

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

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

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

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

2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

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

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

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

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the second law of thermodynamics: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in Table 15.4.1.

Table 15.4.1: The Second Law of Thermodynamics

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

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

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev}, and the second law may be stated as the following:

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

We may use this equation to predict the spontaneity of a process as illustrated in Example 15.4.1.

Example 15.4.1: Will Ice Spontaneously Melt?

The entropy change for the process

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

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at −10.00 °C? Is it spontaneous at +10.00 °C?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = −6.00 kJ.

At −10.00 °C (263.15 K), the following is true:

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

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

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

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

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

Exercise 15.4.1

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{univ}?

Answer

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

The Third Law of Thermodynamics

The previous section described the various contributions of matter and energy dispersal that contribute to the entropy of a system. With these contributions in mind, consider the entropy of a pure, perfectly crystalline solid possessing no kinetic energy (that is, at

a temperature of absolute zero, 0 K). This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion means there is but one possible location for each identical atom or molecule comprising the crystal (W = 1). According to the Boltzmann equation, the entropy of this system is zero.

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

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

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

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

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

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

is computed as:

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

A partial listing of standard entropies is provided in Table 15.4.2, and additional values are provided in Appendix G. The example exercises that follow demonstrate the use of $S°$ values in calculating standard entropy changes for physical and chemical processes.

Table 15.4.2: Standard entropies for selected substances measured at 1 atm and 298.15 K. (Values are approximately equal to those measured at 1 bar, the currently accepted standard state pressure.)

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

Substance	($J\ mol^{-1}\ K^{-1}$)
oxygen	
$O_2(g)$	205.03

Example 15.4.2: Determination of ΔS°

Calculate the standard entropy change for the following process:

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

Solution

Calculate the entropy change using standard entropies as shown above:

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

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

Exercise 15.4.2

Calculate the standard entropy change for the following process:

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

Answer

$-120.6\ J\ K^{-1}\ mol^{-1}$

Example 15.4.3: Determination of ΔS°

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

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

Solution

Calculate the entropy change using standard entropies as shown above:

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

$$[2mol \times S^\circ(CO_2(g)) + 4mol \times S^\circ(H_2O(l))] - [2mol \times S^\circ(CH_3OH(l)) + 3mol \times S^\circ(O_2(g))]$$

$$= \{[2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.2)]\} = -161.6J/K$$

Exercise 15.4.3

Calculate the standard entropy change for the following reaction:

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

Answer

24.7 J/K

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15.5: Free Energy

Learning Objectives

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

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate free energy change for a process using free energies of formation for its reactants and products
- Calculate free energy change for a process using enthalpies of formation and the entropies for its reactants and products
- Explain how temperature affects the spontaneity of some processes
- Relate standard free energy changes to equilibrium constants

One of the challenges of using the second law of thermodynamics to determine if a process is spontaneous is that it requires measurements of the entropy change for the system *and* the entropy change for the surroundings. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the **Gibbs free energy** (G) (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS$$

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

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

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

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

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

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

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

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

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

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

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

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ}. Table 15.5.1 summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Table 15.5.1: Relation between Process Spontaneity and Signs of Thermodynamic Properties

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

What's "Free" about ΔG?

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

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

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

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

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

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

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

Calculating Free Energy Change

Free energy is a state function, so its value depends only on the conditions of the initial and final states of the system. A convenient and common approach to the calculation of free energy changes for physical and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute **standard free energy changes**, ΔG^o, according to the following relation.

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

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

✔ Example 15.5.1: Using Standard Enthalpy and Entropy Changes to Calculate ΔG°

Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for ΔG^o say about the spontaneity of this process?

Solution

The process of interest is the following:

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

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

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

From Appendix G:

Substance	$\Delta H_f^\circ (\mathrm{kJ/mol})$	$S^\circ (\mathrm{kJ/K\ mol})$
$H_2O(l)$	−285.83	70.0
$H_2O(g)$	−241.82	188.8

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

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

Substitution into the standard free energy equation yields:

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

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

? Exercise 15.5.1

Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for $\Delta G°$ say about the spontaneity of this process?

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

Answer

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

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

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

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

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

✓ Example 15.5.2: Using Standard Free Energies of Formation to Calculate ΔG°

Consider the decomposition of yellow mercury(II) oxide.

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

Calculate the standard free energy change at room temperature, using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous under standard conditions?

Solution

The required data are available in Appendix G and are shown here.

Compound	ΔG_f° (kJ / mol)	ΔH_f° (kJ / mol)	S° (kJ / K mol)
HgO (*s*, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
$O_2(g)$	0	0	205.2

(a) Using free energies of formation:

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

(b) Using enthalpies and entropies of formation:

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

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

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

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is nonspontaneous (*not* spontaneous) at room temperature.

? Exercise 15.5.1

Calculate $\Delta G°$ using (a) free energies of formation and (b) enthalpies of formation and entropies (Appendix G). Do the results indicate the reaction to be spontaneous or nonspontaneous at 25 °C?

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

Answer

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

Free Energy Changes for Coupled Reactions

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

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

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

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

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

$$\mathrm{ZnS(s) \rightarrow Zn(s) + S(s)} \quad \Delta G_1^\circ = 201.3kJ$$

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

$$\mathrm{S(s) + O_2(g) \rightarrow SO_2(g)} \quad \Delta G_2^\circ = -300.1kJ$$

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

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

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

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

Example 15.5.3: Calculating Free Energy Change for a Coupled Reaction

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

Solution

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

Decomposition of zinc sulfide:	$\mathrm{ZnS(s) \rightarrow Zn(s) + S(s)}$	$\Delta G_1^\circ = 201.3$ kJ
Formation of hydrogen sulfide:	$\mathrm{S(s) + H_2(g) \rightarrow H_2S(g)}$	$\Delta G_1^\circ = -33.4$ kJ
Coupled reaction:	$\mathrm{ZnS(s) + H_2(g) \rightarrow Zn(s) + H_2S(g)}$	$\Delta G^\circ = 201.3 \text{ kJ} + -33.4 \text{ kJ} = 167.9 \text{ kJ}$

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

Exercise 15.5.3

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

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

Answer

−199.7 kJ; spontaneous

Temperature Dependence of Spontaneity and Extent of Reaction

As was previously demonstrated in this chapter's section on entropy, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. In a similar, but not identical fashion, some chemical reactions can switch from being product-favored at equilibrium, to being reactant-favored at equilibrium, depending on the temperature.

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

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

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

The extent of a process, as reflected in the arithmetic sign of its standard free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (Kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

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

These four scenarios are summarized in Table 15.5.1

Table 15.5.1

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

Sign of ΔH^o	Sign of ΔS^o	Sign of ΔG^o	Temperature Dependence of ΔG^o
+	+	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.

Example 15.5.3: Predicting the Temperature Dependence of Spontaneity

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

$$2\,\mathrm{C}(s) + \mathrm{O}_2(g) \longrightarrow 2\,\mathrm{CO}(g)$$

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

Solution

Combustion processes are exothermic ($\Delta H^\circ < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S^\circ > 0$). The reaction is therefore product-favored at equilibrium ($\Delta G^\circ < 0$) at all temperatures.

Exercise 15.5.3

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

$$4\,\mathrm{Fe}(s) + 3\,\mathrm{O}_2(g) \longrightarrow 2\,\mathrm{Fe}_2\mathrm{O}_3(s)$$

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

Answer

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

When considering the conclusions drawn regarding the temperature dependence of the sign of ΔG^o, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is reactant-favored at equilibrium at one temperature but product-favored at equilibrium at another temperature will necessarily undergo a change in “extent” (as reflected by its ΔG^o) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which ΔG^o is plotted on the y axis versus T on the x axis:

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

$$y = b + mx$$

Such a plot is shown in Figure 15.5.2 A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependence for the sign of ΔG^o as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG^o) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the x-intercept of the line, that is, the value of T for which ΔG^o is zero:

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

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

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

Note

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

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

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

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

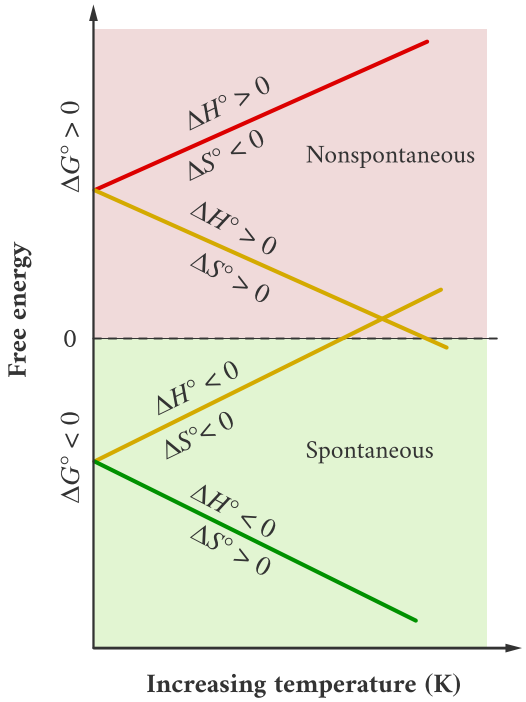


Figure 15.5.2: These plots show the variation in ΔG° with temperature for the four possible combinations of arithmetic sign for ΔH° and ΔS°. Note that in this graph of ΔG°, "spontaneous" is synonymous with "product-favored at equilibrium", and "nonspontaneous" is synonymous with "reactant-favored at equilibrium".

Example 15.5.4: Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its solid and liquid phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in Tables T1 or T2 to estimate the boiling point of water.

Solution

The process of interest is the following phase change:

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

When this process is at equilibrium, $\Delta G = 0$, so the following is true:

$$0 = \Delta H^\circ - T\Delta S^\circ \qquad \text{or} \qquad T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Using the standard thermodynamic data from Tables T1 or T2,

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

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

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

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K (Tables T1 or T2.). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

Exercise 15.5.4

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

Answer

313 K (accepted value 319 K).

Free Energy and Equilibrium

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

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

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

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

R is the gas constant (8.314 J/K mol), T is the kelvin or absolute temperature, and Q is the reaction quotient. For gas phase equilibria, the pressure-based reaction quotient, Q_P, is used. The concentration-based reaction quotient, Q_C, is used for condensed phase equilibria. This equation may be used to predict the spontaneity for a process under any given set of conditions as illustrated in Example 15.5.6

Example 15.5.6: Calculating ΔG under Nonstandard Conditions

What is the free energy change for the process shown here

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

under the specified conditions?

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

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

Solution

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

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

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

Exercise 15.5.6

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

Answer

ΔG = –123.5 kJ/mol; yes

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

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

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

or

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

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in Table 15.5.2

Table 15.5.2: Relations between Standard Free Energy Changes and Equilibrium Constants

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

Example 15.5.7: Calculating an Equilibrium Constant using Standard Free Energy Change

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

Solution

The reaction of interest is the following:

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

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

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

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

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

This result is in reasonable agreement with the value provided in Appendix J.

? Exercise 15.5.7

Use the thermodynamic data provided in Appendix G to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Answer

$K = 3.1$

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy versus the extent of the reaction (for example, as reflected in the value of Q), equilibrium is established when the system's free energy is minimized (Figure 15.5.3). If a system consists of reactants and products in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

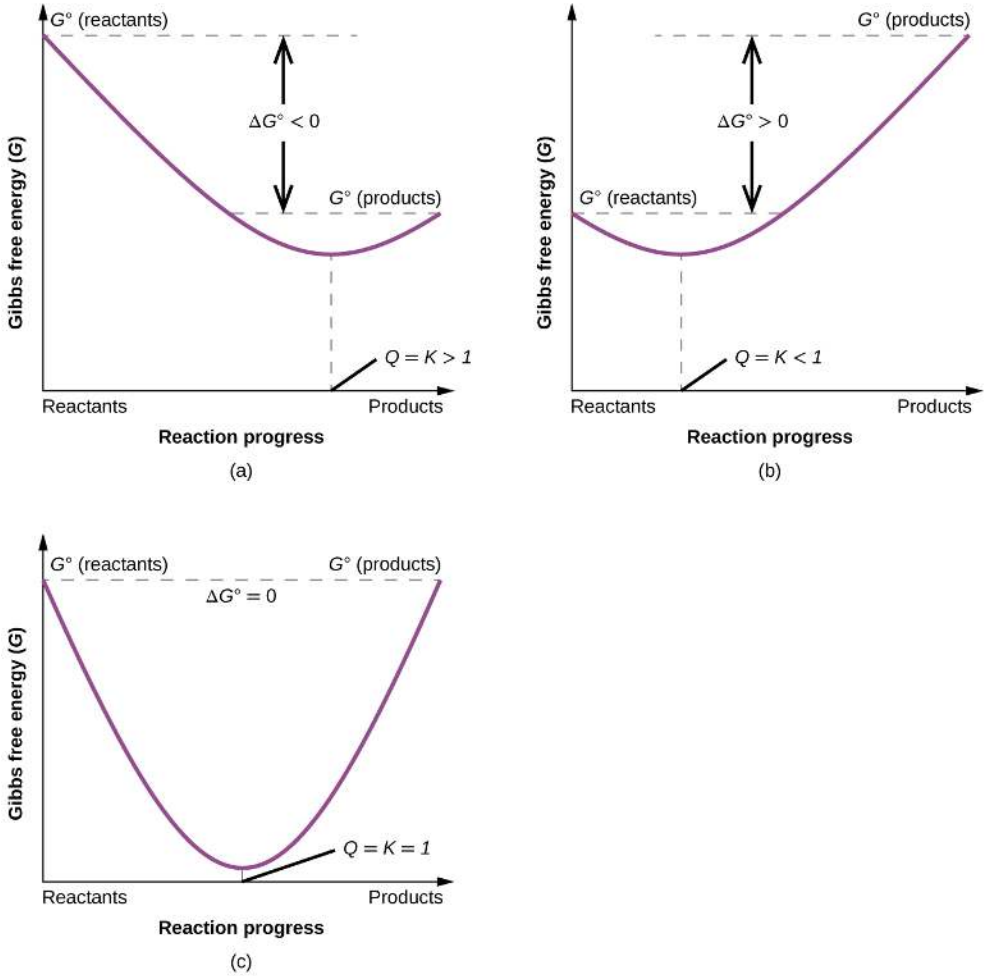


Figure 15.5.3: These plots show the free energy versus reaction progress for systems whose standard free energy changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium.

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15.6: Key Terms

entropy (*S*) | state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates; often described as a measure of the disorder of the system

Gibbs free energy change (*G*) | thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in *G*

microstate | possible configuration or arrangement of matter and energy within a system

nonspontaneous process | process that requires continual input of energy from an external source

reversible process | process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes

second law of thermodynamics | all spontaneous processes involve an increase in the entropy of the universe

spontaneous change | process that takes place without a continuous input of energy from an external source

standard entropy (*S*°) | entropy for one mole of a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K

standard entropy change (Δ*S*°) | change in entropy for a reaction calculated using the standard entropies

standard free energy change (Δ*G*°) | change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

standard free energy of formation | change in free energy accompanying the formation of one mole of substance from its elements in their standard states

third law of thermodynamics | entropy of a perfect crystal at absolute zero (0 K) is zero

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15.7: Key Equations

$$S = k \ln W$$

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

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

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15.8: 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.

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, entropy depends on phase with $S_{solid} < S_{liquid} < S_{gas}$. For different substances in the same 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 and physical changes may be reliably predicted.

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.

Gibbs free energy (G) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A negative value for ΔG indicates a spontaneous process; a positive ΔG indicates a nonspontaneous process; and a ΔG of zero indicates that the system is at equilibrium. A number of approaches to the computation of free energy changes are possible.

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15.9: Exercises

1.

What is a spontaneous reaction?

2.

What is a nonspontaneous reaction?

3.

Indicate whether the following processes are spontaneous or nonspontaneous.

a. (f) Iron rusting in a moist atmosphere

4.

A helium-filled balloon spontaneously deflates overnight as He atoms diffuse through the wall of the balloon. Describe the redistribution of matter and/or energy that accompanies this process.

5.

Many plastic materials are organic polymers that contain carbon and hydrogen. The oxidation of these plastics in air to form carbon dioxide and water is a spontaneous process; however, plastic materials tend to persist in the environment. Explain.

6.

In Figure 16.8 all possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, if the particles are initially evenly distributed between the two boxes, but upon redistribution all end up in Box (b).

7.

In Figure 16.8 all of the possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, for the system when it is converted from distribution (b) to distribution (d).

8.

How does the process described in the previous item relate to the system shown in Figure 16.4?

9.

Consider a system similar to the one in Figure 16.8, except that it contains six particles instead of four. What is the probability of having all the particles in only one of the two boxes in the case? Compare this with the similar probability for the system of four particles that we have derived to be equal to What does this comparison tell us about even larger systems?

10.

Consider the system shown in Figure 16.9. What is the change in entropy for the process where the energy is initially associated only with particle A, but in the final state the energy is distributed between two different particles?

11.

Consider the system shown in Figure 16.9. What is the change in entropy for the process where the energy is initially associated with particles A and B, and the energy is distributed between two particles in different boxes (one in A-B, the other in C-D)?

12.

Arrange the following sets of systems in order of increasing entropy. Assume one mole of each substance and the same temperature for each member of a set.

a. $H_2(g)$, $HBrO_4(g)$, $HBr(g)$
b. $H_2O(l)$, $H_2O(g)$, $H_2O(s)$
c. $He(g)$, $Cl_2(g)$, $P_4(g)$

13.

At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2. Explain.

14.

Consider two processes: sublimation of $I_2(s)$ and melting of $I_2(s)$ (Note: the latter process can occur at the same temperature but somewhat higher pressure).

Is ΔS positive or negative in these processes? In which of the processes will the magnitude of the entropy change be greater?

15.

Indicate which substance in the given pairs has the higher entropy value. Explain your choices.

a. $C_2H_5OH(l)$ or $C_3H_7OH(l)$
b. $C_2H_5OH(l)$ or $C_2H_5OH(g)$
c. $2H(g)$ or $H(g)$

16.

Predict the sign of the entropy change for the following processes.

a. An ice cube is warmed to near its melting point.
b. Exhaled breath forms fog on a cold morning.
c. Snow melts.

17.

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

a.
b.
c.

18.

Write the balanced chemical equation for the combustion of methane, $CH_4(g)$, to give carbon dioxide and water vapor. Explain why it is difficult to predict whether ΔS is positive or negative for this chemical reaction.

19.

Write the balanced chemical equation for the combustion of benzene, $C_6H_6(l)$, to give carbon dioxide and water vapor. Would you expect ΔS to be positive or negative in this process?

20.

What is the difference between ΔS and $\Delta S°$ for a chemical change?

21.

Calculate for the following changes.

a. (f)

22.

Determine the entropy change for the combustion of liquid ethanol, C_2H_5OH, under the standard conditions to give gaseous carbon dioxide and liquid water.

23.

Determine the entropy change for the combustion of gaseous propane, C_3H_8, under the standard conditions to give gaseous carbon dioxide and water.

24.

“Thermite” reactions have been used for welding metal parts such as railway rails and in metal refining. One such thermite reaction is Is the reaction spontaneous at room temperature under standard conditions? During the reaction, the surroundings absorb 851.8 kJ/mol of heat.

25.

Using the relevant values listed in Appendix G, calculate for the following changes:

a.
b.

26.

From the following information, determine for the following:

27.

By calculating ΔS_{univ} at each temperature, determine if the melting of 1 mole of NaCl(s) is spontaneous at 500 °C and at 700 °C.

What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

28.

Use the standard entropy data in Appendix G to determine the change in entropy for each of the following reactions. All the processes occur at the standard conditions and 25 °C.

a. (f)

29.

Use the standard entropy data in Appendix G to determine the change in entropy for each of the following reactions. All the processes occur at the standard conditions and 25 °C.

a. (f)

30.

What is the difference between ΔG and $\Delta G°$ for a chemical change?

31.

A reaction has = 100 kJ/mol and Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

32.

Explain what happens as a reaction starts with $\Delta G < 0$ (negative) and reaches the point where $\Delta G = 0$.

33.

Use the standard free energy of formation data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

a. (f)

34.

Use the standard free energy data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

a. (f)

35.

Given:

a. Determine the standard free energy of formation, for phosphoric acid.
b. How does your calculated result compare to the value in Appendix G? Explain.

36.

Is the formation of ozone ($O_3(g)$) from oxygen ($O_2(g)$) spontaneous at room temperature under standard state conditions?

37.

Consider the decomposition of red mercury(II) oxide under standard state conditions.

a. Is the decomposition spontaneous under standard state conditions?
b. Above what temperature does the reaction become spontaneous?

38.

Among other things, an ideal fuel for the control thrusters of a space vehicle should decompose in a spontaneous exothermic reaction when exposed to the appropriate catalyst. Evaluate the following substances under standard state conditions as suitable candidates for fuels.

a. Ammonia:
b. Diborane:
c. Hydrazine:
d. Hydrogen peroxide:

39.

Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

a. (f)

40.

Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

a. (f)

41.

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

a.
b.
c.
d.
e.

42.

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

a.
b.
c.
d.
e.

43.

Calculate the equilibrium constant at the temperature given.

a.
b.
c.
d.
e.

44.

Calculate the equilibrium constant at the temperature given.

a.
b.
c.
d.
e.

45.

Consider the following reaction at 298 K:

What is the standard free energy change at this temperature? Describe what happens to the initial system, where the reactants and products are in standard states, as it approaches equilibrium.

46.

Determine the normal boiling point (in kelvin) of dichloromethane, CH_2Cl_2. Find the actual boiling point using the Internet or some other source, and calculate the percent error in the temperature. Explain the differences, if any, between the two values.

47.

Under what conditions is spontaneous?

48.

At room temperature, the equilibrium constant (K_w) for the self-ionization of water is 1.00 10^{-14}. Using this information, calculate the standard free energy change for the aqueous reaction of hydrogen ion with hydroxide ion to produce water. (Hint: The reaction is the reverse of the self-ionization reaction.)

49.

Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

50.

Consider the decomposition of $CaCO_3(s)$ into $CaO(s)$ and $CO_2(g)$. What is the equilibrium partial pressure of CO_2 at room temperature?

51.

In the laboratory, hydrogen chloride ($HCl(g)$) and ammonia ($NH_3(g)$) often escape from bottles of their solutions and react to form the ammonium chloride ($NH_4Cl(s)$), the white glaze often seen on glassware. Assuming that the number of moles of each gas that escapes into the room is the same, what is the maximum partial pressure of HCl and NH_3 in the laboratory at room temperature? (Hint: The partial pressures will be equal and are at their maximum value when at equilibrium.)

52.

Benzene can be prepared from acetylene. Determine the equilibrium constant at 25 °C and at 850 °C. Is the reaction spontaneous at either of these temperatures? Why is all acetylene not found as benzene?

53.

Carbon dioxide decomposes into CO and O_2 at elevated temperatures. What is the equilibrium partial pressure of oxygen in a sample at 1000 °C for which the initial pressure of CO_2 was 1.15 atm?

54.

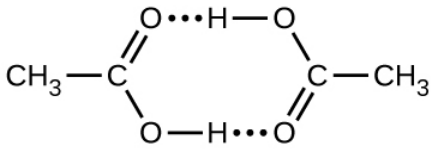
Carbon tetrachloride, an important industrial solvent, is prepared by the chlorination of methane at 850 K.

What is the equilibrium constant for the reaction at 850 K? Would the reaction vessel need to be heated or cooled to keep the temperature of the reaction constant?

55.

Acetic acid, CH_3CO_2H, can form a dimer, $(CH_3CO_2H)_2$, in the gas phase.

The dimer is held together by two hydrogen bonds with a total strength of 66.5 kJ per mole of dimer.



At 25 °C, the equilibrium constant for the dimerization is 1.3 10^3 (pressure in atm). What is $\Delta S°$ for the reaction?

56.

Determine $\Delta G°$ for the following reactions.

(a) Antimony pentachloride decomposes at 448 °C. The reaction is:

An equilibrium mixture in a 5.00 L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2.

(b) Chlorine molecules dissociate according to this reaction:

1.00% of Cl_2 molecules dissociate at 975 K and a pressure of 1.00 atm.

57.

Given that the for $Pb^{2+}(aq)$ and $Cl^{-}(aq)$ is −24.3 kJ/mole and −131.2 kJ/mole respectively, determine the solubility product, K_{sp}, for $PbCl_2(s)$.

58.

Determine the standard free energy change, for the formation of $S^{2-}(aq)$ given that the for $Ag^{+}(aq)$ and $Ag_2S(s)$ are 77.1 kJ/mole and −39.5 kJ/mole respectively, and the solubility product for $Ag_2S(s)$ is $8\ 10^{-51}$.

59.

Determine the standard enthalpy change, entropy change, and free energy change for the conversion of diamond to graphite. Discuss the spontaneity of the conversion with respect to the enthalpy and entropy changes. Explain why diamond spontaneously changing into graphite is not observed.

60.

The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.

a. Is the evaporation of water under standard thermodynamic conditions spontaneous?
b. Determine the equilibrium constant, K_P, for this physical process.
c. By calculating ΔG, determine if the evaporation of water at 298 K is spontaneous when the partial pressure of water, is 0.011 atm.
d. If the evaporation of water were always nonspontaneous at room temperature, wet laundry would never dry when placed outside. In order for laundry to dry, what must be the value of in the air?

61.

In glycolysis, the reaction of glucose (Glu) to form glucose-6-phosphate (G6P) requires ATP to be present as described by the following equation:

In this process, ATP becomes ADP summarized by the following equation:

Determine the standard free energy change for the following reaction, and explain why ATP is necessary to drive this process:

62.

One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):

a. Is the reaction spontaneous or nonspontaneous under standard thermodynamic conditions?
b. Standard thermodynamic conditions imply the concentrations of G6P and F6P to be 1 *M*, however, in a typical cell, they are not even close to these values. Calculate ΔG when the concentrations of G6P and F6P are 120 μ*M* and 28 μ*M* respectively, and discuss the spontaneity of the forward reaction under these conditions. Assume the temperature is 37 °C.

63.

Without doing a numerical calculation, determine which of the following will reduce the free energy change for the reaction, that is, make it less positive or more negative, when the temperature is increased. Explain.

a.
b.
c.
d.

64.

When ammonium chloride is added to water and stirred, it dissolves spontaneously and the resulting solution feels cold. Without doing any calculations, deduce the signs of ΔG, ΔH, and ΔS for this process, and justify your choices.

65.

An important source of copper is from the copper ore, chalcocite, a form of copper(I) sulfide. When heated, the Cu_2S decomposes to form copper and sulfur described by the following equation:

a. Determine for the decomposition of $Cu_2S(s)$.
b. The reaction of sulfur with oxygen yields sulfur dioxide as the only product. Write an equation that describes this reaction, and determine for the process.
c. The production of copper from chalcocite is performed by roasting the Cu_2S in air to produce the Cu. By combining the equations from Parts (a) and (b), write the equation that describes the roasting of the chalcocite, and explain why coupling these reactions together makes for a more efficient process for the production of the copper.

66.

What happens to (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

a.
b.
c.

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CHAPTER OVERVIEW

16: Electrochemistry

Electrochemistry deals with chemical reactions that produce electricity and the changes associated with the passage of electrical current through matter. The reactions involve electron transfer, and so they are oxidation-reduction (or redox) reactions. Many metals may be purified or electroplated using electrochemical methods. Devices such as automobiles, smartphones, electronic tablets, watches, pacemakers, and many others use batteries for power. Batteries use chemical reactions that produce electricity spontaneously and that can be converted into useful work. All electrochemical systems involve the transfer of electrons in a reacting system. In many systems, the reactions occur in a region known as the cell, where the transfer of electrons occurs at electrodes.

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16.1: Introduction

Another chapter in this text introduced the chemistry of reduction-oxidation (redox) reactions. This important reaction class is defined by changes in oxidation states for one or more reactant elements, and it includes a subset of reactions involving the transfer of electrons between reactant species. Around the turn of the nineteenth century, chemists began exploring ways these electrons could be transferred *indirectly* via an external circuit rather than directly via intimate contact of redox reactants. In the two centuries since, the field of *electrochemistry* has evolved to yield significant insights on the fundamental aspects of redox chemistry as well as a wealth of technologies ranging from industrial-scale metallurgical processes to robust, rechargeable batteries for electric vehicles (Figure 16.1.1). In this chapter, the essential concepts of electrochemistry will be addressed.



Figure 16.1.1: Electric vehicles are powered by batteries, devices that harness the energy of spontaneous redox reactions. (credit: modification of work by Robert Couse-Baker)

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16.2: Summary

Redox reactions are defined by changes in reactant oxidation numbers, and those most relevant to electrochemistry involve actual transfer of electrons. Aqueous phase redox processes often involve water or its characteristic ions, H^+ and OH^-, as reactants in addition to the oxidant and reductant, and equations representing these reactions can be challenging to balance. The half-reaction method is a systematic approach to balancing such equations that involves separate treatment of the oxidation and reduction half-reactions.

Galvanic cells are devices in which a spontaneous redox reaction occurs indirectly, with the oxidant and reductant redox couples contained in separate half-cells. Electrons are transferred from the reductant (in the anode half-cell) to the oxidant (in the cathode half-cell) through an external circuit, and inert solution phase ions are transferred between half-cells, through a salt bridge, to maintain charge neutrality. The construction and composition of a galvanic cell may be succinctly represented using chemical formulas and others symbols in the form of a cell schematic (cell notation).

The property of potential, E, is the energy associated with the separation/transfer of charge. In electrochemistry, the potentials of cells and half-cells are thermodynamic quantities that reflect the driving force or the spontaneity of their redox processes. The cell potential of an electrochemical cell is the difference in between its cathode and anode. To permit easy sharing of half-cell potential data, the standard hydrogen electrode (SHE) is assigned a potential of exactly 0 V and used to define a single electrode potential for any given half-cell. The electrode potential of a half-cell, E_X, is the cell potential of said half-cell acting as a cathode when connected to a SHE acting as an anode. When the half-cell is operating under standard state conditions, its potential is the standard electrode potential, $E°_X$. Standard electrode potentials reflect the relative oxidizing strength of the half-reaction's reactant, with stronger oxidants exhibiting larger (more positive) $E°_X$ values. Tabulations of standard electrode potentials may be used to compute standard cell potentials, $E°_{cell}$, for many redox reactions. The arithmetic sign of a cell potential indicates the spontaneity of the cell reaction, with positive values for spontaneous reactions and negative values for nonspontaneous reactions (spontaneous in the reverse direction).

Potential is a thermodynamic quantity reflecting the intrinsic driving force of a redox process, and it is directly related to the free energy change and equilibrium constant for the process. For redox processes taking place in electrochemical cells, the maximum (electrical) work done by the system is easily computed from the cell potential and the reaction stoichiometry and is equal to the free energy change for the process. The equilibrium constant for a redox reaction is logarithmically related to the reaction's cell potential, with larger (more positive) potentials indicating reactions with greater driving force that equilibrate when the reaction has proceeded far towards completion (large value of K). Finally, the potential of a redox process varies with the composition of the reaction mixture, being related to the reactions standard potential and the value of its reaction quotient, Q, as described by the Nernst equation.

Galvanic cells designed specifically to function as electrical power supplies are called batteries. A variety of both single-use batteries (primary cells) and rechargeable batteries (secondary cells) are commercially available to serve a variety of applications, with important specifications including voltage, size, and lifetime. Fuel cells, sometimes called flow batteries, are devices that harness the energy of spontaneous redox reactions normally associated with combustion processes. Like batteries, fuel cells enable the reaction's electron transfer via an external circuit, but they require continuous input of the redox reactants (fuel and oxidant) from an external reservoir. Fuel cells are typically much more efficient in converting the energy released by the reaction to useful work in comparison to internal combustion engines.

Spontaneous oxidation of metals by natural electrochemical processes is called corrosion, familiar examples including the rusting of iron and the tarnishing of silver. Corrosion process involve the creation of a galvanic cell in which different sites on the metal object function as anode and cathode, with the corrosion taking place at the anodic site. Approaches to preventing corrosion of metals include use of a protective coating of zinc (galvanization) and the use of sacrificial anodes connected to the metal object (cathodic protection).

Nonspontaneous redox processes may be forced to occur in electrochemical cells by the application of an appropriate potential using an external power source—a process known as electrolysis. Electrolysis is the basis for certain ore refining processes, the industrial production of many chemical commodities, and the electroplating of metal coatings on various products. Measurement of the current flow during electrolysis permits stoichiometric calculations.

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16.3: Exercises

1.

Identify each half-reaction below as either oxidation or reduction.

a.
b.
c.
d.

2.

Identify each half-reaction below as either oxidation or reduction.

a.
b.
c.
d.

3.

Assuming each pair of half-reactions below takes place in an acidic solution, write a balanced equation for the overall reaction.

a.
b.
c.
d.

4.

Balance the equations below assuming they occur in an acidic solution.

a.
b.
c.

5.

Identify the oxidant and reductant of each reaction of the previous exercise.

6.

Balance the equations below assuming they occur in a basic solution.

a.
b.
c.
d.

7.

Identify the oxidant and reductant of each reaction of the previous exercise.

8.

Why don’t hydroxide ions appear in equations for half-reactions occurring in acidic solution?

9.

Why don’t hydrogen ions appear in equations for half-reactions occurring in basic solution?

10.

Why must the charge balance in oxidation-reduction reactions?

11.

Write cell schematics for the following cell reactions, using platinum as an inert electrode as needed.

a.

b.
c.
d.

12.

Assuming the schematics below represent galvanic cells as written, identify the half-cell reactions occurring in each.

a.
b.

13.

Write a balanced equation for the cell reaction of each cell in the previous exercise.

14.

Balance each reaction below, and write a cell schematic representing the reaction as it would occur in a galvanic cell.

a.
b.
c.
d.

15.

Identify the oxidant and reductant in each reaction of the previous exercise.

16.

From the information provided, use cell notation to describe the following systems:

a. In one half-cell, a solution of $Pt(NO_3)_2$ forms Pt metal, while in the other half-cell, Cu metal goes into a $Cu(NO_3)_2$ solution with all solute concentrations 1 *M*.
b. The cathode consists of a gold electrode in a 0.55 *M* $Au(NO_3)_3$ solution and the anode is a magnesium electrode in 0.75 *M* $Mg(NO_3)_2$ solution.
c. One half-cell consists of a silver electrode in a 1 *M* $AgNO_3$ solution, and in the other half-cell, a copper electrode in 1 *M* $Cu(NO_3)_2$ is oxidized.

17.

Why is a salt bridge necessary in galvanic cells like the one in Figure 17.3?

18.

An active (metal) electrode was found to gain mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode an anode or a cathode? Explain.

19.

An active (metal) electrode was found to lose mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode an anode or a cathode? Explain.

20.

The masses of three electrodes (A, B, and C), each from three different galvanic cells, were measured before and after the cells were allowed to pass current for a while. The mass of electrode A increased, that of electrode B was unchanged, and that of electrode C decreased. Identify each electrode as active or inert, and note (if possible) whether it functioned as anode or cathode.

21.

Calculate the standard cell potential for each reaction below, and note whether the reaction is spontaneous under standard state conditions.

a.
b.
c.
d.

22.

Calculate the standard cell potential for each reaction below, and note whether the reaction is spontaneous under standard state conditions.

a.
b.
c.
d.

23.

Write the balanced cell reaction for the cell schematic below, calculate the standard cell potential, and note whether the reaction is spontaneous under standard state conditions.

24.

Determine the cell reaction and standard cell potential at 25 °C for a cell made from a cathode half-cell consisting of a silver electrode in 1 *M* silver nitrate solution and an anode half-cell consisting of a zinc electrode in 1 *M* zinc nitrate. Is the reaction spontaneous at standard conditions?

25.

Determine the cell reaction and standard cell potential at 25 °C for a cell made from an anode half-cell containing a cadmium electrode in 1 *M* cadmium nitrate and a cathode half-cell consisting of an aluminum electrode in 1 *M* aluminum nitrate solution. Is the reaction spontaneous at standard conditions?

26.

Write the balanced cell reaction for the cell schematic below, calculate the standard cell potential, and note whether the reaction is spontaneous under standard state conditions.

27.

For each pair of standard cell potential and electron stoichiometry values below, calculate a corresponding standard free energy change (kJ).

a. 0.000 V, n = 2
b. +0.434 V, n = 2
c. −2.439 V, n = 1

28.

For each pair of standard free energy change and electron stoichiometry values below, calculate a corresponding standard cell potential.

a. 12 kJ/mol, n = 3
b. −45 kJ/mol, n = 1

29.

Determine the standard cell potential and the cell potential under the stated conditions for the electrochemical reactions described here. State whether each is spontaneous or nonspontaneous under each set of conditions at 298.15 K.

a.
b. The cell made from an anode half-cell consisting of an aluminum electrode in 0.015 *M* aluminum nitrate solution and a cathode half-cell consisting of a nickel electrode in 0.25 *M* nickel(II) nitrate solution.
c. The cell comprised of a half-cell in which aqueous bromine (1.0 *M*) is being oxidized to bromide ion (0.11 *M*) and a half-cell in which Al^{3+} (0.023 *M*) is being reduced to aluminum metal.

30.

Determine ΔG and $\Delta G°$ for each of the reactions in the previous problem.

31.

Use the data in Appendix L to calculate equilibrium constants for the following reactions. Assume 298.15 K if no temperature is given.

a.
b.
c.
d.

32.

Consider a battery made from one half-cell that consists of a copper electrode in 1 *M* $CuSO_4$ solution and another half-cell that consists of a lead electrode in 1 *M* $Pb(NO_3)_2$ solution.

a. What is the standard cell potential for the battery?
b. What are the reactions at the anode, cathode, and the overall reaction?
c. Most devices designed to use dry-cell batteries can operate between 1.0 and 1.5 V. Could this cell be used to make a battery that could replace a dry-cell battery? Why or why not.
d. Suppose sulfuric acid is added to the half-cell with the lead electrode and some $PbSO_4(s)$ forms. Would the cell potential increase, decrease, or remain the same?

33.

Consider a battery with the overall reaction:

a. What is the reaction at the anode and cathode?
b. A battery is “dead” when its cell potential is zero. What is the value of *Q* when this battery is dead?
c. If a particular dead battery was found to have $[Cu^{2+}] = 0.11$ *M*, what was the concentration of silver ion?

34.

Why do batteries go dead, but fuel cells do not?

35.

Use the Nernst equation to explain the drop in voltage observed for some batteries as they discharge.

36.

Using the information thus far in this chapter, explain why battery-powered electronics perform poorly in low temperatures.

37.

Which member of each pair of metals is more likely to corrode (oxidize)?

a. Mg or Ca
b. Au or Hg
c. Fe or Zn
d. Ag or Pt

38.

Consider the following metals: Ag, Au, Mg, Ni, and Zn. Which of these metals could be used as a sacrificial anode in the cathodic protection of an underground steel storage tank? Steel is an alloy composed mostly of iron, so use −0.447 V as the standard reduction potential for steel.

39.

Aluminum is more easily oxidized than iron and yet when both are exposed to the environment, untreated aluminum has very good corrosion resistance while the corrosion resistance of untreated iron is poor. What might explain this observation?

40.

If a sample of iron and a sample of zinc come into contact, the zinc corrodes but the iron does not. If a sample of iron comes into contact with a sample of copper, the iron corrodes but the copper does not. Explain this phenomenon.

41.

Suppose you have three different metals, A, B, and C. When metals A and B come into contact, B corrodes and A does not corrode. When metals A and C come into contact, A corrodes and C does not corrode. Based on this information, which metal corrodes and which metal does not corrode when B and C come into contact?

42.

Why would a sacrificial anode made of lithium metal be a bad choice

43.

If a 2.5 A current flows through a circuit for 35 minutes, how many coulombs of charge moved through the circuit?

44.

For the scenario in the previous question, how many electrons moved through the circuit?

45.

Write the half-reactions and cell reaction occurring during electrolysis of each molten salt below.

a. $CaCl_2$
b. LiH
c. $AlCl_3$
d. $CrBr_3$

46.

What mass of each product is produced in each of the electrolytic cells of the previous problem if a total charge of 3.33 10^5 C passes through each cell?

47.

How long would it take to reduce 1 mole of each of the following ions using the current indicated?

a. Al^{3+}, 1.234 A
b. Ca^{2+}, 22.2 A
c. Cr^{5+}, 37.45 A
d. Au^{3+}, 3.57 A

48.

A current of 2.345 A passes through the cell shown in Figure 17.19 for 45 minutes. What is the volume of the hydrogen collected at room temperature if the pressure is exactly 1 atm? (Hint: Is hydrogen the only gas present above the water?)

49.

An irregularly shaped metal part made from a particular alloy was galvanized with zinc using a $Zn(NO_3)_2$ solution. When a current of 2.599 A was used, it took exactly 1 hour to deposit a 0.01123-mm layer of zinc on the part. What was the total surface area of the part? The density of zinc is 7.140 g/cm^3.

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16.4: Review of Redox Chemistry

Learning Objectives

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

- Describe defining traits of redox chemistry
- Identify the oxidant and reductant of a redox reaction
- Balance chemical equations for redox reactions using the half-reaction method

Since reactions involving electron transfer are essential to the topic of electrochemistry, a brief review of redox chemistry is provided here that summarizes and extends the content of an earlier text chapter (see chapter on reaction stoichiometry). Readers wishing additional review are referred to the text chapter on reaction stoichiometry.

Oxidation Numbers

By definition, a redox reaction is one that entails changes in *oxidation number* (or *oxidation state*) for one or more of the elements involved. The oxidation number of an element in a compound is essentially an assessment of how the electronic environment of its atoms is different in comparison to atoms of the pure element. By this description, *the oxidation number of an atom in an element is equal to zero*. For an atom in a compound, *the oxidation number is equal to the charge the atom would have in the compound if the compound were ionic*. Consequential to these rules, *the sum of oxidation numbers for all atoms in a molecule is equal to the charge on the molecule*. To illustrate this formalism, examples from the two compound classes, ionic and covalent, will be considered.

Simple ionic compounds present the simplest examples to illustrate this formalism, since by definition the elements' oxidation numbers are numerically equivalent to ionic charges. Sodium chloride, NaCl, is comprised of Na^+ cations and Cl^- anions, and so oxidation numbers for sodium and chlorine are, +1 and −1, respectively. Calcium fluoride, CaF_2, is comprised of Ca^{2+} cations and F^- anions, and so oxidation numbers for calcium and fluorine are, +2 and −1, respectively.

Covalent compounds require a more challenging use of the formalism. Water is a covalent compound whose molecules consist of two H atoms bonded separately to a central O atom via polar covalent O−H bonds. The shared electrons comprising an O−H bond are more strongly attracted to the more electronegative O atom, and so it acquires a partial negative charge in the water molecule (relative to an O atom in elemental oxygen). Consequently, H atoms in a water molecule exhibit partial positive charges compared to H atoms in elemental hydrogen. The sum of the partial negative and partial positive charges for each water molecule is zero, and the water molecule is neutral.

Imagine that the polarization of shared electrons within the O−H bonds of water were 100% complete—the result would be *transfer* of electrons from H to O, and water would be an ionic compound comprised of O^{2-} anions and H^+ cations. And so, the oxidations numbers for oxygen and hydrogen in water are −2 and +1, respectively. Applying this same logic to carbon tetrachloride, CCl_4, yields oxidation numbers of +4 for carbon and −1 for chlorine. In the nitrate ion, NO_3^-, the oxidation number for nitrogen is +5 and that for oxygen is −2, summing to equal the 1− charge on the molecule:

$$(1N\text{ atom})\left(\frac{+5}{N\text{ atom}}\right)+(3O\text{ atoms})\left(\frac{-2}{O\text{ atom}}\right)=+5+-6=-1$$

Balancing Redox Equations

The unbalanced equation below describes the decomposition of molten sodium chloride:

$$\mathrm{NaCl(l)}\longrightarrow\mathrm{Na(l)}+\mathrm{Cl_2(g)}\qquad\text{(unbalanced)}$$

This reaction satisfies the criterion for redox classification, since the oxidation number for Na is decreased from +1 to 0 (it undergoes *reduction*) and that for Cl is increased from −1 to 0 (it undergoes *oxidation*). The equation in this case is easily balanced by inspection, requiring stoichiometric coefficients of 2 for the NaCl and Na:

$$2\,\mathrm{NaCl(l)}\longrightarrow2\,\mathrm{Na(l)}+\mathrm{Cl_2(g)}\qquad\text{(balanced)}$$

Redox reactions that take place in aqueous solutions are commonly encountered in electrochemistry, and many involve water or its characteristic ions, $H^+(aq)$ and $OH^-(aq)$, as reactants or products. In these cases, equations representing the redox reaction can be

very challenging to balance by inspection, and the use of a systematic approach called the *half-reaction method* is helpful.

Balancing REDOX reactions via the half-reaction Method

This approach involves the following steps:

1. Write skeletal equations for the oxidation and reduction half-reactions.
2. Balance each half-reaction for all elements except H and O.
3. Balance each half-reaction for O by adding H_2O.
4. Balance each half-reaction for H by adding H^+.
5. Balance each half-reaction for charge by adding electrons.
6. If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.
7. Add the two half-reactions and simplify.
8. If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

The examples below demonstrate the application of this method to balancing equations for aqueous redox reactions.

Example 16.4.1: Balancing Equations for Redox Reactions in Acidic Solutions

Write the balanced equation representing reaction between solid copper and nitric acid to yield aqueous copper(II) ions and nitrogen monoxide gas.

Solution

Following the steps of the half-reaction method:

Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\text{oxidation:} \quad \mathrm{Cu(s) \longrightarrow Cu^{2+}(aq)}$$

$$\text{reduction:} \quad \mathrm{HNO_3(aq) \longrightarrow NO(g)}$$

Step 2: Balance each half-reaction for all elements except H and O.

$$\text{oxidation:} \quad \mathrm{Cu(s) \longrightarrow Cu^{2+}(aq)}$$

$$\text{reduction:} \quad \mathrm{HNO_3(aq) \longrightarrow NO(g)}$$

Step 3: Balance each half-reaction for O by adding H_2O.

$$\text{oxidation:} \quad \mathrm{Cu(s) \longrightarrow Cu^{2+}(aq)}$$

$$\text{reduction:} \quad \mathrm{HNO_3(aq) \longrightarrow NO(g) + \mathbf{2\,H_2O(l)}}$$

Step 4: Balance each half-reaction for H by adding H^+.

$$\text{oxidation:} \quad \mathrm{Cu(s) \longrightarrow Cu^{2+}(aq)}$$

$$\text{reduction:} \quad \mathrm{\mathbf{3\,H^+(aq)} + HNO_3(aq) \longrightarrow NO(g) + 2\,H_2O(l)}$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\text{oxidation:} \quad \mathrm{Cu(s) \longrightarrow Cu^{2+}(aq) + \mathbf{2\,e^-}}$$

$$\text{reduction:} \quad \mathrm{\mathbf{3\,e^-} + 3\,H^+(aq) + HNO_3(aq) \longrightarrow NO(g) + 2\,H_2O(l)}$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.

$$\text{oxidation } (\times 3): \quad \mathrm{\mathbf{3}\,Cu(s) \longrightarrow \mathbf{3}\,Cu^{2+}(aq) + \mathbf{6}\ \cancel{2}e^-}$$

$$\text{reduction } (\times 2): \quad \mathrm{\mathbf{6}\ \cancel{3}e^- + \mathbf{6}\ \cancel{3}H^+(aq) + \mathbf{2}\,HNO_3(aq) \longrightarrow \mathbf{2}\,NO(g) + \mathbf{4}\ \cancel{2}H_2O(l)}$$

Step 7: Add the two half-reactions and simplify.

$$3\,Cu(s) + \cancel{6\,e^-} + 6\,H^+(aq) + 2\,HNO_3(aq) \longrightarrow 3\,Cu^{2+}(aq) + \cancel{6\,e^-} + 2\,NO(g) + 4\,H_2O(l)$$

$$3\,Cu(s) + 6\,H^+(aq) + 2\,HNO_3(aq) \longrightarrow 3\,Cu^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l)$$

Step 8: If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

This step not necessary since the solution is stipulated to be acidic.

The balanced equation for the reaction in an acidic solution is then

$$3\,Cu(s) + 6\,H^+(aq) + 2\,HNO_3(aq) \longrightarrow 3\,Cu^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l)$$

Exercise 16.4.1

The reaction above results when using relatively diluted nitric acid. If concentrated nitric acid is used, nitrogen dioxide is produced instead of nitrogen monoxide. Write a balanced equation for this reaction.

Answer

$$Cu(s) + 2\,H^+(aq) + 2\,HNO_3(aq) \longrightarrow Cu^{2+}(aq) + 2\,NO_2(g) + 2\,H_2O(l)$$

Example 16.4.2: Balancing Equations for Redox Reactions in Basic Solutions

Write the balanced equation representing reaction between aqueous permanganate ion, , and solid chromium(III) hydroxide, $Cr(OH)_3$, to yield solid manganese(IV) oxide, MnO_2, and aqueous chromate ion, The reaction takes place in a basic solution.

Solution

Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\text{oxidation:} \quad Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq)$$

$$\text{reduction:} \quad MnO_4^-(aq) \longrightarrow MnO_2(s)$$

Step 2: Balance each half-reaction for all elements except H and O.

$$\text{oxidation:} \quad Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq)$$

$$\text{reduction:} \quad MnO_4^-(aq) \longrightarrow MnO_2(s)$$

Step 3: Balance each half-reaction for O by adding H_2O.

$$\text{oxidation:} \quad \mathbf{H_2O(l)} + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq)$$

$$\text{reduction:} \quad MnO_4^-(aq) \longrightarrow MnO_2(s) + \mathbf{2\,H_2O(l)}$$

Step 4: Balance each half-reaction for H by adding H^+.

$$\text{oxidation:} \quad H_2O(l) + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) + \mathbf{5\,H^+(aq)}$$

$$\text{reduction:} \quad \mathbf{4\,H^+(aq)} + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l)$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\text{oxidation:} \quad H_2O(l) + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) + 5\,H^+(aq) + \mathbf{3\,e^-}$$

$$\text{reduction:} \quad \mathbf{3\,e^-} + 4\,H^+(aq) + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l)$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.

This step is not necessary since the number of electrons is already in balance.

Step 7: Add the two half-reactions and simplify.

$$\cancel{H_2O(l)} + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) + \cancel{5}\,^{1}H^+(aq) + \cancel{3e^-}$$

$$+ \quad \cancel{3e^-} + \cancel{4\,H^+(aq)} + MnO_4^-(aq) \longrightarrow MnO_2(s) + \cancel{2}\,^{1}H_2O(l)$$

$$Cr(OH)_3(s) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + H^+(aq) + H_2O(l)$$

Step 8: If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

$$OH^-(aq) + Cr(OH)_3(s) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + \cancel{H^+(aq)} + H_2O(l) + \cancel{OH^-(aq)}$$

after neutralizing the H^+, we get the balanced equation for the reaction in a basic solution

$$OH^-(aq) + Cr(OH)_3(s) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + 2\,H_2O(l)$$

? Exercise 16.4.2

Aqueous permanganate ion may also be reduced using aqueous bromide ion, Br^-, the products of this reaction being solid manganese(IV) oxide and aqueous bromate ion, BrO_3^-. Write the balanced equation for this reaction occurring in a basic medium.

Answer

$$H_2O(l) + 2\,MnO_4^-(aq) + Br^-(aq) \longrightarrow 2\,MnO_2(s) + BrO_3^-(aq) + 2\,OH^-(aq)$$

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16.5: Galvanic Cells

Learning Objectives

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

- Describe the function of a galvanic cell and its components
- Use cell notation to symbolize the composition and construction of galvanic cells

As demonstration of spontaneous chemical change, Figure 16.5.1: shows the result of immersing a coiled wire of copper into an aqueous solution of silver nitrate. A gradual but visually impressive change spontaneously occurs as the initially colorless solution becomes increasingly blue, and the initially smooth copper wire becomes covered with a porous gray solid.



Figure 16.5.1: A copper wire and an aqueous solution of silver nitrate (left) are brought into contact (center) and a spontaneous transfer of electrons occurs, creating blue $Cu^{2+}(aq)$ and gray $Ag(s)$ (right).

These observations are consistent with (i) the oxidation of elemental copper to yield copper(II) ions, $Cu^{2+}(aq)$, which impart a blue color to the solution, and (ii) the reduction of silver(I) ions to yield elemental silver, which deposits as a fluffy solid on the copper wire surface. And so, *the direct transfer of electrons from the copper wire to the aqueous silver ions is spontaneous* under the employed conditions. A summary of this redox system is provided by these equations:

Consider the construction of a device that contains all the reactants and products of a redox system like the one here, but prevents physical contact between the reactants. Direct transfer of electrons is, therefore, prevented; transfer, instead, takes place indirectly through an external circuit that contacts the separated reactants. Devices of this sort are generally referred to as *electrochemical cells*, and those in which a spontaneous redox reaction takes place are called galvanic cells (or voltaic cells).

A galvanic cell based on the spontaneous reaction between copper and silver(I) is depicted in Figure 16.5.2 The cell is comprised of two half-cells, each containing the redox conjugate pair (“couple”) of a single reactant. The half-cell shown at the left contains the Cu(0)/Cu(II) couple in the form of a solid copper foil and an aqueous solution of copper nitrate. The right half-cell contains the Ag(I)/Ag(0) couple as solid silver foil and an aqueous silver nitrate solution. An external circuit is connected to each half-cell at its solid foil, meaning the Cu and Ag foil each function as an *electrode*. By definition, the anode of an electrochemical cell is the electrode at which oxidation occurs (in this case, the Cu foil) and the cathode is the electrode where reduction occurs (the Ag foil). The redox reactions in a galvanic cell occur only at the interface between each half-cell’s reaction mixture and its electrode. To keep the reactants separate while maintaining charge-balance, the two half-cell solutions are connected by a tube filled with inert electrolyte solution called a salt bridge. The spontaneous reaction in this cell produces Cu^{2+} cations in the anode half-cell and consumes Ag^{+} ions in the cathode half-cell, resulting in a compensatory flow of inert ions from the salt bridge that maintains charge balance. Increasing concentrations of Cu^{2+} in the anode half-cell are balanced by an influx of NO_3^{-} from the salt bridge, while a flow of Na^{+} into the cathode half-cell compensates for the decreasing Ag^{+} concentration.

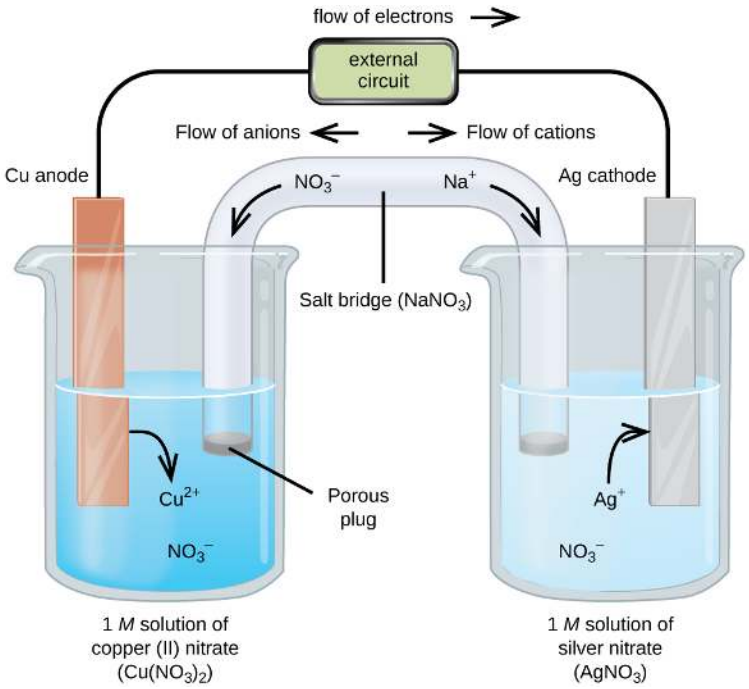


Figure 16.5.2: A galvanic cell based on the spontaneous reaction between copper and silver(I) ions.

Cell Notation

Abbreviated symbolism is commonly used to represent a galvanic cell by providing essential information on its composition and structure. These symbolic representations are called cell notations or cell schematics, and they are written following a few guidelines:

- The relevant components of each half-cell are represented by their chemical formulas or element symbols
- All interfaces between component phases are represented by vertical parallel lines; if two or more components are present in the same phase, their formulas are separated by commas
- By convention, the schematic begins with the anode and proceeds left-to-right identifying phases and interfaces encountered within the cell, ending with the cathode

A verbal description of the cell as viewed from anode-to-cathode is often a useful first-step in writing its schematic. For example, the galvanic cell shown in Figure 16.5.2 consists of a solid copper anode immersed in an aqueous solution of copper(II) nitrate that is connected via a salt bridge to an aqueous silver(I) nitrate solution, immersed in which is a solid silver cathode. Converting this statement to symbolism following the above guidelines results in the cell schematic:

Consider a different galvanic cell (see Figure 16.5.3) based on the spontaneous reaction between solid magnesium and aqueous iron(III) ions:

In this cell, a solid magnesium anode is immersed in an aqueous solution of magnesium chloride that is connected via a salt bridge to an aqueous solution containing a mixture of iron(III) chloride and iron(II) chloride, immersed in which is a platinum cathode. The cell schematic is then written as

Notice the cathode half-cell is different from the others considered thus far in that its electrode is comprised of a substance (Pt) that is neither a reactant nor a product of the cell reaction. This is required when neither member of the half-cell's redox couple can reasonably function as an electrode, which must be electrically conductive and in a phase separate from the half-cell solution. In this case, both members of the redox couple are solute species, and so Pt is used as an inert electrode that can simply provide or accept electrons to redox species in solution. Electrodes constructed from a member of the redox couple, such as the Mg anode in this cell, are called active electrodes.

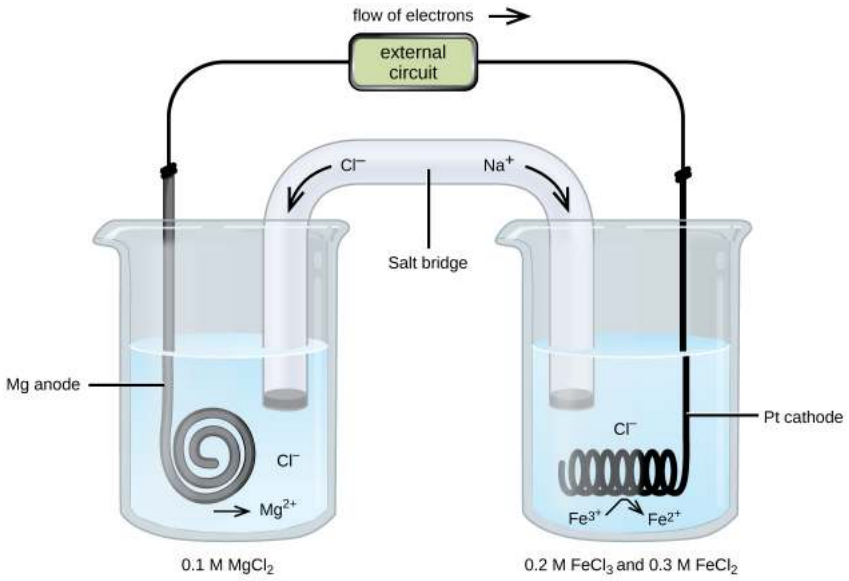


Figure 16.5.3: A galvanic cell based on the spontaneous reaction between magnesium and iron(III) ions.

Example 16.5.1: Writing Galvanic Cell Schematics

A galvanic cell is fabricated by connecting two half-cells with a salt bridge, one in which a chromium wire is immersed in a 1 M $CrCl_3$ solution and another in which a copper wire is immersed in 1 M $CuCl_2$. Assuming the chromium wire functions as an anode, write the schematic for this cell along with equations for the anode half-reaction, the cathode half-reaction, and the overall cell reaction.

Solution

Since the chromium wire is stipulated to be the anode, the schematic begins with it and proceeds left-to-right, symbolizing the other cell components until ending with the copper wire cathode:

The half-reactions for this cell are

Multiplying to make the number of electrons lost by Cr and gained by Cu^{2+} equal yields

Adding the half-reaction equations and simplifying yields an equation for the cell reaction:

Exercise 16.5.1

Omitting solute concentrations and spectator ion identities, write the schematic for a galvanic cell whose net cell reaction is shown below.

Answer

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16.6: Electrode and Cell Potentials

Learning Objectives

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

- Describe and relate the definitions of electrode and cell potentials
- Interpret electrode potentials in terms of relative oxidant and reductant strengths
- Calculate cell potentials and predict redox spontaneity using standard electrode potentials

Unlike the spontaneous oxidation of copper by aqueous silver(I) ions described previously, immersing a copper wire in an aqueous solution of lead(II) ions yields no reaction. The two species, $Ag^{+}(aq)$ and $Pb^{2+}(aq)$, thus show a distinct difference in their redox activity towards copper: the silver ion spontaneously oxidized copper, but the lead ion did not. Electrochemical cells permit this relative redox activity to be quantified by an easily measured property, *potential*. This property is more commonly called *voltage* when referenced in regard to electrical applications, and it is a measure of energy accompanying the transfer of charge. Potentials are measured in the volt unit, defined as one joule of energy per one coulomb of charge, V = J/C.

When measured for purposes of electrochemistry, a potential reflects the driving force for a specific type of charge transfer process, namely, the transfer of electrons between redox reactants. Considering the nature of potential in this context, it is clear that the potential of a single half-cell or a single electrode can't be measured; "transfer" of electrons requires both a donor and recipient, in this case a reductant and an oxidant, respectively. Instead, a half-cell potential may only be assessed relative to that of another half-cell. It is only the *difference in potential* between two half-cells that may be measured, and these measured potentials are called cell potentials, E_{cell}, defined as

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

where $E_{cathode}$ and E_{anode} are the potentials of two different half-cells functioning as specified in the subscripts. As for other thermodynamic quantities, the standard cell potential, $E°_{cell}$, is a cell potential measured when both half-cells are under standard-state conditions (1 *M* concentrations, 1 bar pressures, 298 K):

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

To simplify the collection and sharing of potential data for half-reactions, the scientific community has designated one particular half-cell to serve as a universal reference for cell potential measurements, assigning it a potential of exactly 0 V. This half-cell is the **standard hydrogen electrode** (SHE) and it is based on half-reaction below:

$$2\,\mathrm{H^+(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2(g)}$$

A typical SHE contains an inert platinum electrode immersed in precisely 1 *M* aqueous H^+ and a stream of bubbling H_2 gas at 1 bar pressure, all maintained at a temperature of 298 K (see Figure 16.6.1).

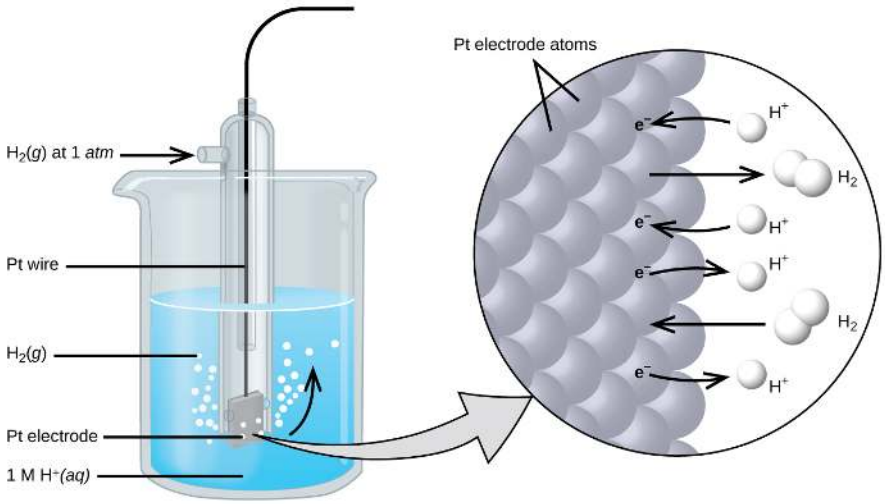


Figure 16.6.1: A standard hydrogen electrode (SHE).

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The assigned potential of the SHE permits the definition of a conveniently measured potential for a single half-cell. The electrode potential (E_X) for a half-cell *X* is defined as *the potential measured for a cell comprised of X acting as cathode and the SHE acting as anode*:

$$E_{\text{cell}} = E_X - E_{SHE}$$
$$E_{SHE} = 0V \text{ (defined)}$$
$$E_{\text{cell}} = E_X$$

When the half-cell *X* is under standard-state conditions, its potential is the standard electrode potential, $E°_X$. Since the definition of cell potential requires the half-cells function as cathodes, these potentials are sometimes called *standard reduction potentials*.

This approach to measuring electrode potentials is illustrated in Figure 16.6.2 , which depicts a cell comprised of an SHE connected to a copper(II)/copper(0) half-cell under standard-state conditions. A voltmeter in the external circuit allows measurement of the potential difference between the two half-cells. Since the Cu half-cell is designated as the cathode in the definition of cell potential, it is connected to the red (positive) input of the voltmeter, while the designated SHE anode is connected to the black (negative) input. These connections insure that the sign of the measured potential will be consistent with the sign conventions of electrochemistry per the various definitions discussed above. A cell potential of +0.337 V is measured, and so

$$E°_{\text{cell}} = E°_{\text{Cu}} = +0.337V$$

Tabulations of E° values for other half-cells measured in a similar fashion are available as reference literature to permit calculations of cell potentials and the prediction of the spontaneity of redox processes.

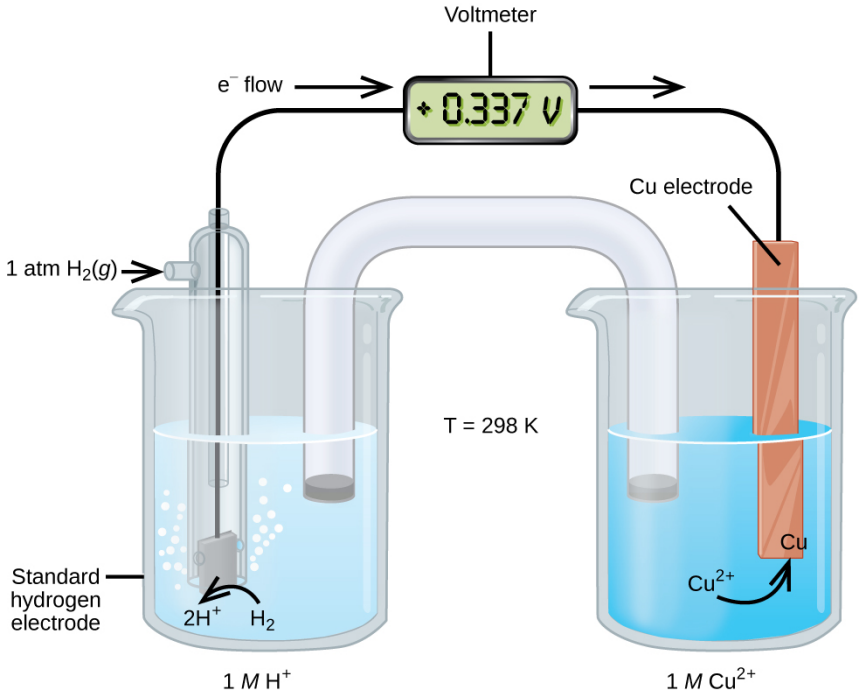


Figure 16.6.2: A cell permitting experimental measurement of the standard electrode potential for the half-reaction

Table 16.6.1 provides a listing of standard electrode potentials for a selection of half-reactions in numerical order, and a more extensive alphabetical listing is given in Appendix L.

Table 16.6.1: Selected Standard Reduction Potentials at 25 °C

Half-Reaction	*E*° (V)
$\mathrm{F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)}$	+2.866
$\mathrm{PbO_2(s) + SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)}$	+1.69
$\mathrm{MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)}$	+1.507

Half-Reaction	$E°$ (V)
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.498
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.35827
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+1.229
$Pt^{2+}(aq) + 2e^- \longrightarrow Pt(s)$	+1.20
$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$	+1.0873
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.7996
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.7973
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.558
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.5355
$NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq)$	+0.26808
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22233
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.151
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	-0.1262
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	-0.1375
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	-0.257
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	-0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	-0.3505
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	-0.4030
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	-0.447
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	-0.744
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	-1.185
$Zn(OH)_2(s) + 2e^- \longrightarrow Zn(s) + 2OH^-(aq)$	-1.245
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	-0.7618
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	-1.662
$Mg_2(aq) + 2e^- \longrightarrow Mg(s)$	-2.372
$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	-2.868
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	-2.912
$K^+(aq) + e^- \longrightarrow K(s)$	-2.931
$K^+(aq) + e^- \longrightarrow K(s)$	-3.04

Example 16.6.1: Calculating Standard Cell Potentials

What is the standard potential of the galvanic cell shown in Figure 17.3?

Solution

The cell in Figure 17.3 is galvanic, the spontaneous cell reaction involving oxidation of its copper anode and reduction of silver(I) ions at its silver cathode:

$$\begin{array}{lll} \text{anode:} & \mathrm{Cu(s) \longrightarrow Cu^{2+} + 2\,e^-} & \\ \text{cathode:} & \mathrm{2\,Ag^+(aq) + 2\,e^- \longrightarrow 2\,Ag(s)} & \\ \hline \text{cell:} & \mathrm{Cu(s) + 2\,Ag^+(aq) \longrightarrow Cu^{2+} + 2\,Ag(s)} & E^o_{\text{cell}} = 0\,\text{V} \end{array}$$

The standard cell potential computed as

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{Ag} - E^\circ_{Cu} \\ &= 0.7996V - 0.34V \\ &= +0.46V \end{aligned}$$

Exercise

What is the standard cell potential expected if the silver cathode half-cell in Figure 17.3 is replaced with a lead half-cell:

$$\mathrm{Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)}$$

Answer

−0. 47 V

Intrepreting Electrode and Cell Potentials

Thinking carefully about the definitions of cell and electrode potentials and the observations of spontaneous redox change presented thus far, a significant relation is noted. The previous section described the spontaneous oxidation of copper by aqueous silver(I) ions, but no observed reaction with aqueous lead(II) ions. Results of the calculations in Example 16.6.1 have just shown *the spontaneous process is described by a positive cell potential* while *the nonspontaneous process exhibits a negative cell potential*. And so, with regard to the relative effectiveness ("strength") with which aqueous Ag^+ and Pb^{2+} ions oxidize Cu under standard conditions, *the stronger oxidant is the one exhibiting the greater standard electrode potential, E°*. Since by convention electrode potentials are for reduction processes, an increased value of E^o corresponds to an increased driving force behind the reduction of the species (hence increased effectiveness of its action as an *oxidizing agent* on some other species). Negative values for electrode potentials are simply a consequence of assigning a value of 0 V to the SHE, indicating the reactant of the half-reaction is a weaker oxidant than aqueous hydrogen ions.

Applying this logic to the numerically ordered listing of standard electrode potentials in Table 16.6.1 shows this listing to be likewise in order of the oxidizing strength of the half-reaction's reactant species, decreasing from strongest oxidant (most positive *E°*) to weakest oxidant (most negative *E°*). Predictions regarding the spontaneity of redox reactions under standard state conditions can then be easily made by simply comparing the relative positions of their table entries. By definition, $E°_{\text{cell}}$ is positive when $E^o_{\text{cathode}} > E^o_{\text{anode}}$, and so any redox reaction in which the oxidant's entry is above the reductant's entry is predicted to be spontaneous.

Reconsideration of the two redox reactions in Example 16.6.1 provides support for this fact. The entry for the silver(I)/silver(0) half-reaction is above that for the copper(II)/copper(0) half-reaction, and so the oxidation of Cu by Ag^+ is predicted to be spontaneous ($E°_{\text{cathode}} > E°_{\text{anode}}$ and so $E°_{\text{cell}} > 0$). Conversely, the entry for the lead(II)/lead(0) half-cell is beneath that for copper(II)/copper(0), and the oxidation of Cu by Pb^{2+} is nonspontaneous ($E°_{\text{cathode}} < E°_{\text{anode}}$ and so $E°_{\text{cell}} < 0$).

Recalling the chapter on thermodynamics, the spontaneities of the forward and reverse reactions of a reversible process show a reciprocal relationship: if a process is spontaneous in one direction, it is non-spontaneous in the opposite direction. As an indicator of spontaneity for redox reactions, the potential of a cell reaction shows a consequential relationship in its arithmetic sign. The spontaneous oxidation of copper by lead(II) ions is *not* observed,

$$\mathrm{Cu(s) + Pb^{2+}(aq) \longrightarrow Cu^{2+}(aq) + Pb(s)} \quad E^\circ_{\text{forward}} = -0.47\ \mathrm{V (negative, non-spontaneous)}$$

and so the reverse reaction, the oxidation of lead by copper(II) ions, is predicted to occur spontaneously:

$$\mathrm{Pb(s) + Cu^{2+}(aq) \longrightarrow Pb^{2+}(aq) + Cu(s)} \quad E^\circ_{\text{forward}} = +0.47\ \mathrm{V (positive, spontaneous)}$$

Note that reversing the direction of a redox reaction effectively interchanges the identities of the cathode and anode half-reactions, and so the cell potential is calculated from electrode potentials in the reverse subtraction order than that for the forward reaction. In practice, a voltmeter would report a potential of −0.47 V with its red and black inputs connected to the Pb and Cu electrodes, respectively. If the inputs were swapped, the reported voltage would be +0.47 V.

Example 16.6.2: Predicting Redox Spontaneity

Are aqueous iron(II) ions predicted to spontaneously oxidize elemental chromium under standard state conditions? Assume the half-reactions to be those available in Table 16.6.1.

Solution

Referring to the tabulated half-reactions, the redox reaction in question can be represented by the equations below:

$$\mathrm{Cr(s) + Fe^{2+}(aq) \longrightarrow Cr^{3+}(aq) + Fe(s)}$$

The entry for the putative oxidant, Fe^{2+}, appears *above* the entry for the reductant, Cr, and so a spontaneous reaction is predicted per the quick approach described above. Supporting this predication by calculating the standard cell potential for this reaction gives

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{\text{Fe(II)}} - E^\circ_{\text{Cr}} \\ &= -0.447V - -0.744V = +0.297V \end{aligned}$$

The positive value for the standard cell potential indicates the process is spontaneous under standard state conditions.

Exercise

Use the data in Table 16.6.1 to predict the spontaneity of the oxidation of bromide ion by molecular iodine under standard state conditions, supporting the prediction by calculating the standard cell potential for the reaction. Repeat for the oxidation of iodide ion by molecular bromine.

Answer

$$\begin{aligned} \mathrm{I_2(s) + 2\,Br^-(aq)} &\longrightarrow \mathrm{2\,I^-(aq) + Br_2(l)} \qquad E_{\text{cell}} = -0.5518\ \mathrm{V\ (nonspontaneous)} \\ \mathrm{Br_2(s) + 2\,I^-(aq)} &\longrightarrow \mathrm{2\,Br^-(aq) + I_2(l)} \qquad E^\circ_{\text{cell}} = +0.5518\ \mathrm{V\ (spontaneous)} \end{aligned}$$

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16.7: Potential, Free Energy, and Equilibrium

Learning Objectives

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

- Explain the relations between potential, free energy change, and equilibrium constants
- Perform calculations involving the relations between cell potentials, free energy changes, and equilibrium
- Use the Nernst equation to determine cell potentials under nonstandard conditions

So far in this chapter, the relationship between the cell potential and reaction *spontaneity* has been described, suggesting a link to the free energy change for the reaction (see chapter on thermodynamics). The interpretation of potentials as measures of oxidant *strength* was presented, bringing to mind similar measures of acid-base strength as reflected in equilibrium constants (see the chapter on acid-base equilibria). This section provides a summary of the relationships between potential and the related thermodynamic properties ΔG and K.

E° and ΔG°

The standard free energy change of a process, ΔG°, was defined in a previous chapter as the maximum work that could be performed by a system, w_{max}. In the case of a redox reaction taking place within a galvanic cell under standard state conditions, essentially all the work is associated with transferring the electrons from reductant-to-oxidant, w_{elec}:

$$\Delta G^\circ = w_{\text{max}} = w_{\text{elec}}$$

The work associated with transferring electrons is determined by the total amount of charge (coulombs) transferred and the cell potential:

$$\Delta G^\circ = w_{\text{elec}} = -nFE^\circ_{\text{cell}}$$

where n is the number of moles of electrons transferred, F is **Faraday's constant**, and E°_{cell} is the standard cell potential. The relation between free energy change and standard cell potential confirms the sign conventions and spontaneity criteria previously discussed for both of these properties: spontaneous redox reactions exhibit positive potentials and negative free energy changes.

E° and K

Combining a previously derived relation between ΔG° and K (see the chapter on thermodynamics) and the equation above relating ΔG° and $E°_{\text{cell}}$ yields the following:

$$\Delta G^\circ = -RT\ln K = -nFE^\circ_{\text{cell}} \tag{16.7.1}$$

with

$$E^\circ_{\text{coll}} = \left(\frac{RT}{nF}\right)\ln K$$

This equation indicates redox reactions with large (positive) standard cell potentials will proceed far towards completion, reaching equilibrium when the majority of reactant has been converted to product. A summary of the relations between $E°$, $\Delta G°$ and K is depicted in Figure 16.7.1, and a table correlating reaction spontaneity to values of these properties is provided in Table 16.7.1.

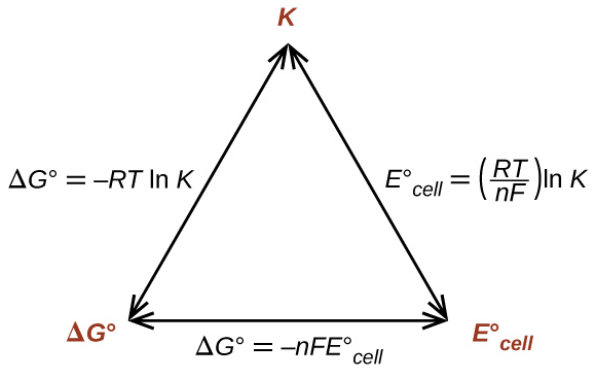


Figure 16.7.1: Graphic depicting the relation between three important thermodynamic properties.

Table 16.7.1

K	$\Delta G°$	$E°_{\text{cell}}$	Comment
> 1	< 0	> 0	Reaction is spontaneous under standard conditions Products more abundant at equilibrium
< 1	> 0	< 0	Reaction is non-spontaneous under standard conditions Reactants more abundant at equilibrium
= 1	= 0	= 0	Reaction is at equilibrium under standard conditions Reactants and products equally abundant

Example 16.7.1: Equilibrium Constants, Standard Cell Potentials, and Standard Free Energy Changes

Use data from Appendix L to calculate the standard cell potential, standard free energy change, and equilibrium constant for the following reaction at 25 °C. Comment on the spontaneity of the forward reaction and the composition of an equilibrium mixture of reactants and products.

$$2\,\text{Ag}^+(\text{aq}) + \text{Fe}(\text{s}) \rightleftharpoons 2\,\text{Ag}(\text{s}) + \text{Fe}^{2+}(\text{aq})$$

Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in Appendix L.

anode:	$\text{Fe}(\text{s}) \longrightarrow \text{Fe}^{2+}(\text{aq}) + 2\,\text{e}^-$	$E^o_{\text{Fe}^{2+}/\text{Fe}} = -0.447\ \text{V}$
cathode:	$2 \times (\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s}))$	$E^o_{\text{Ag}^+/\text{Ag}} = +0.7996\ \text{V}$
cell:	$\text{Fe}(\text{s}) + 2\,\text{Ag}^+(\text{aq}) \longrightarrow \text{Fe}^{2+}(\text{aq}) + 2\,\text{Ag}(\text{s})$	$E^o_{\text{cell}} = +1.2247\ \text{V}$

with

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^o_{\text{Fe}^{2+}/\text{Fe}} - E^o_{\text{Ag}^+/\text{Ag}} = +1.2247\ \text{V}$$

With $n = 2$, the equilibrium constant is then

$$E^\circ_{\text{cell}} = \frac{0.0592V}{n}\log K$$

$$K = 10^{n\times E^\circ_{\text{cal}}/0.0592V}$$

$$= 10^{2\times 1.247V/0.0592V}$$

$$= 10^{42.128}$$

$$= 1.3\times 10^{42}$$

The standard free energy is then Equation 16.7.1

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$= -2\times 96,485\frac{C}{mol}\times 1.247\frac{J}{C} = -240.6\frac{kJ}{mol}$$

The reaction is spontaneous, as indicated by a negative free energy change and a positive cell potential. The *K* value is very large, indicating the reaction proceeds to near completion to yield an equilibrium mixture containing mostly products.

? Exercise 16.7.1

What is the standard free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?

$$\text{Sn(s)} + 2\,\text{Cu}^{2+}\text{(aq)} \rightleftharpoons \text{Sn}^{2+}\text{(aq)} + 2\,\text{Cu}^{+}\text{(aq)}$$

Answer

Spontaneous

$n = 2$

$E^\circ_{\text{cell}} = +0.291V$

$[\Delta G^\circ = -56.2\frac{kJ}{mol}$

K = 6.8 10^9.

Potentials at Nonstandard Conditions: The Nernst Equation

Most of the redox processes that interest science and society do not occur under standard state conditions, and so the potentials of these systems under nonstandard conditions are a property worthy of attention. Having established the relationship between potential and free energy change in this section, the previously discussed relation between free energy change and reaction mixture composition can be used for this purpose.

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

Notice the reaction quotient, *Q*, appears in this equation, making the free energy change dependent upon the composition of the reaction mixture. Substituting the equation relating free energy change to cell potential yields the **Nernst equation**:

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + RT\ln Q$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q$$

This equation describes how the potential of a redox system (such as a galvanic cell) varies from its standard state value, specifically, showing it to be a function of the number of electrons transferred, *n*, the temperature, *T*, and the reaction mixture composition as reflected in *Q*. A convenient form of the Nernst equation for most work is one in which values for the fundamental constants (R and F) and standard temperature (298) K), along with a factor converting from natural to base-10 logarithms, have been included:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592V}{n}\log Q \tag{16.7.2}$$

Example 16.7.2: Predicting Redox Spontaneity Under Nonstandard Conditions

Use the Nernst equation to predict the spontaneity of the redox reaction shown below at room temperature.

$$\mathrm{Co(s) + Fe^{2+}(aq,\ 1.94\ M) \longrightarrow Co^{2+}(aq,\ 0.15\ M) + Fe(s)}$$

Solution

Collecting information from Appendix L and the problem,

anode:	$\mathrm{Co(s) \longrightarrow Co^{2+}(aq) + 2\,e^-}$	$E^o_{\mathrm{Co^{2+}/Co}} = -0.28\ \mathrm{V}$
cathode:	$\mathrm{Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)}$	$E^o_{\mathrm{Fe^{+}/Fe}} = -0.447\ \mathrm{V}$
cell:	$\mathrm{Co(s) + Fe^{2+}(Aq) \longrightarrow Fe(s) + Co^{2+}(aq)}$	$E^o_{\mathrm{cell}} = -0.17\ \mathrm{V}$

with

$$E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{cathode}} - E^\circ_{\mathrm{anode}} = -0.447V - (-0.28V) = -0.17V$$

Notice the negative value of the standard cell potential indicates the process is not spontaneous under standard conditions. Substitution of the Nernst equation terms for the nonstandard conditions requires calculating the reaction quotient Q

$$Q = \frac{\left[\mathrm{Co^{2+}}\right]}{\left[\mathrm{Fe^{2+}}\right]} = \frac{0.15M}{1.94M} = 0.077$$

them Q and n are substituted into Equation \red{Nernst at room temperature}

$$\begin{aligned} E_{\mathrm{cell}} &= E^\circ_{\mathrm{cell}} - \frac{0.0592\ \mathrm{V}}{n}\log Q \\ &= -0.17\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{2}\log 0.077 \\ &= -0.17\ \mathrm{V} + 0.033\ \mathrm{V} \\ &= -0.14\ \mathrm{V} \end{aligned}$$

The cell potential remains negative (slightly) under the specified conditions, and so the reaction remains nonspontaneous.

Exercise 16.7.2

For the cell schematic below at room temperature, identify values for *n* and *Q*, and calculate the cell potential, E_{cell}.

$$\mathrm{Al(s)|Al^{3+}(aq,\ 0.15\ M)|Cu^{2+}(aq,\ 0.025\ M)|Cu(s)}$$

Answer

n = 6; *Q* = 1440; E_{cell} = +1.97 V, spontaneous.

A **concentration cell** is constructed by connecting two nearly identical half-cells, each based on the same half-reaction and using the same electrode, varying only in the concentration of one redox species. The potential of a concentration cell, therefore, is determined only by the difference in concentration of the chosen redox species. The example problem below illustrates the use of the Nernst equation in calculations involving concentration cells.

Example 16.7.3: Concentration Cells

What is the cell potential of the concentration cell operating at room temperature described by

$$\mathrm{Zn(s)|Zn^{2+}(aq,\ 0.10\ M)|Zn^{2+}(aq,\ 0.50\ M)|Zn(s)}$$

Solution

From the information given:

anode:	$\mathrm{Zn(s) \longrightarrow Zn^{2+}(aq,\ 0.10\ M) + 2\,e^-}$	$E^o_{\mathrm{Co^{2+}/Co}} = -0.7618\ \mathrm{V}$
cathode:	$\mathrm{Zn^{2+}(aq,\ 0.50\ M) + 2\,e^- \longrightarrow Zn(s)}$	$E^o_{\mathrm{Fe^{+}/Fe}} = -0,7618\ \mathrm{V}$
cell:	$\mathrm{\cancel{Zn(s)} + Zn^{2+}(aq,\ 0.50\ M) \longrightarrow Zn^{2+}(aq,\ 0.10\ M) + \cancel{Zn(s)}}$	$E^o_{\mathrm{cell}} = 0\ \mathrm{V}$

Substituting into the Nernst equation (Equation 16.7.2),

$$E_{\mathrm{cell}} = 0.000\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{2}\log\frac{0.10}{0.50} = +0.021\ \mathrm{V}$$

The positive value for cell potential indicates the overall cell reaction (see above) is spontaneous. This spontaneous reaction is one in which the zinc ion concentration in the cathode falls (it is reduced to elemental zinc) while that in the anode rises (it is produced by oxidation of the zinc anode). A greater driving force for zinc reduction is present in the cathode, where the zinc(II) ion concentration is greater ($E_{\mathrm{cathode}} > E_{\mathrm{anode}}$).

Exercise 16.7.1

The concentration cell above was allowed to operate until the cell reaction reached equilibrium at room temperature. What are the cell potential and the concentrations of zinc(II) in each half-cell for the cell now?

Answer

E_{cell} = 0.000 V; $[Zn^{2+}]_{\mathrm{cathode}} = [Zn^{2+}]_{\mathrm{anode}}$ = 0.30 *M*

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16.8: Batteries and Fuel Cells

Learning Objectives

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

- Describe the electrochemistry associated with several common batteries
- Distinguish the operation of a fuel cell from that of a battery

There are many technological products associated with the past two centuries of electrochemistry research, none more immediately obvious than the battery. A **battery** is a galvanic cell that has been specially designed and constructed in a way that best suits its intended use a source of electrical power for specific applications. Among the first successful batteries was the *Daniell cell*, which relied on the spontaneous oxidation of zinc by copper(II) ions (Figure 16.8.1):

$$\mathrm{Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)}$$

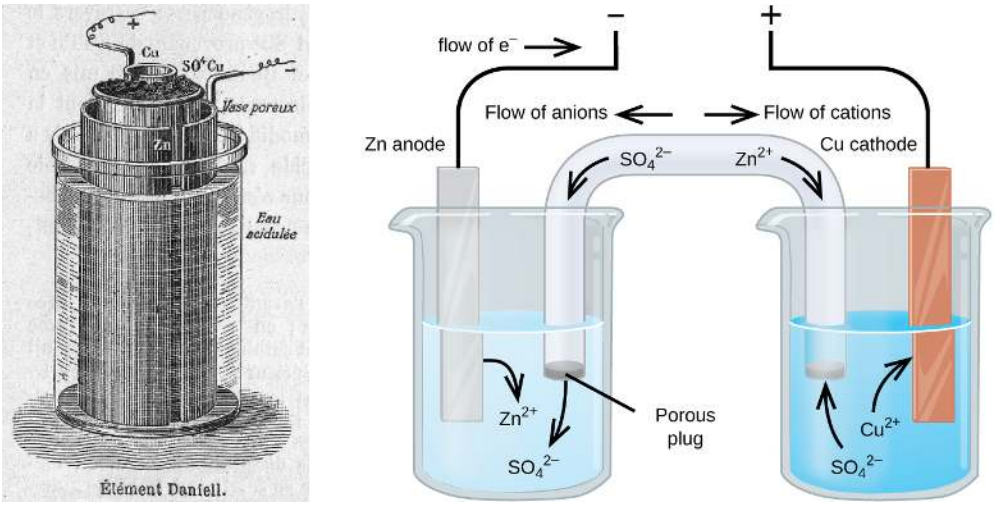


Figure 16.8.1: Illustration of a Daniell cell taken from a 1904 journal publication (left) along with a simplified illustration depicting the electrochemistry of the cell (right). The 1904 design used a porous clay pot to both contain one of the half-cell's content and to serve as a salt bridge to the other half-cell.

Modern batteries exist in a multitude of forms to accommodate various applications, from tiny button batteries that provide the modest power needs of a wristwatch to the very large batteries used to supply backup energy to municipal power grids. Some batteries are designed for single-use applications and cannot be recharged (primary cells), while others are based on conveniently reversible cell reactions that allow recharging by an external power source (secondary cells). This section will provide a summary of the basic electrochemical aspects of several batteries familiar to most consumers, and will introduce a related electrochemical device called a *fuel cell* that can offer improved performance in certain applications.

Link to Learning

Visit this site to learn more about batteries.

Single-Use Batteries

A common primary battery is the dry cell, which uses a zinc can as both container and anode ("–" terminal) and a graphite rod as the cathode ("+" terminal). The Zn can is filled with an electrolyte paste containing manganese(IV) oxide, zinc(II) chloride, ammonium chloride, and water. A graphite rod is immersed in the electrolyte paste to complete the cell. The spontaneous cell reaction involves the oxidation of zinc:

$$\mathrm{Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-} \qquad \text{(anode)}$$

and the reduction of manganese(IV)

$$2\,MnO_2(s) + 2\,NH_4Cl(aq) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,NH_3(aq) + H_2O(l) + 2\,Cl^- \qquad \text{(cathode)}$$

which together yield the cell reaction:

$$2\,MnO_2(s) + 2\,NH_4Cl(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2\,NH_3(aq) + H_2O(l) + 2\,Cl^- \qquad \text{(cell)}$$

The voltage (*cell potential*) of a dry cell is approximately 1.5 V. Dry cells are available in various sizes (e.g., D, C, AA, AAA). All sizes of dry cells comprise the same components, and so they exhibit the same voltage, but larger cells contain greater amounts of the redox reactants and therefore are capable of transferring correspondingly greater amounts of charge. Like other galvanic cells, dry cells may be connected in series to yield batteries with greater voltage outputs, if needed.

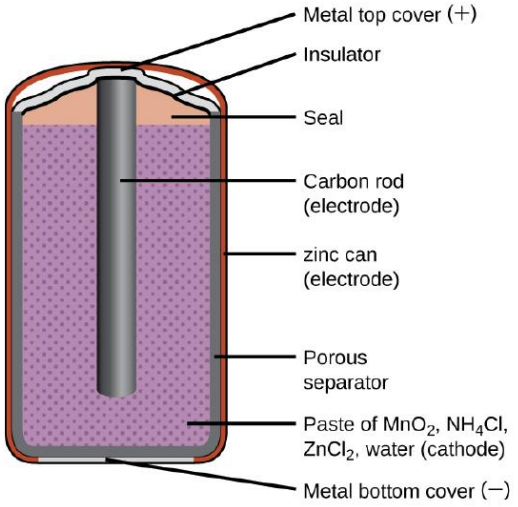


Figure 16.8.2: A schematic diagram shows a typical dry cell.

Link to Learning

Visit this site to learn more about zinc-carbon batteries.

Alkaline batteries (Figure 16.8.3) were developed in the 1950s to improve on the performance of the dry cell, and they were designed around the same redox couples. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are

anode:	$Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^-$	
cathode:	$2\,MnO_2(s) + H_2O(l) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,OH^-(aq)$	
cell:	$Zn(s) + 2\,MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s)$	$E_{cell} = +1.43\ V$

An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so they should be removed from devices for long-term storage. While some alkaline batteries are rechargeable, most are not. Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.

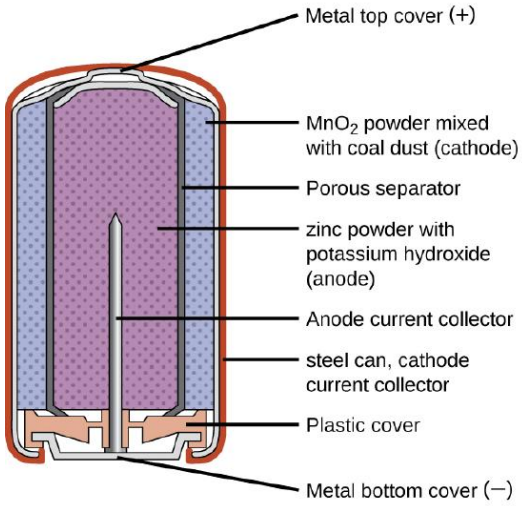


Figure 16.8.3: Alkaline batteries were designed as improved replacements for zinc-carbon (dry cell) batteries.

Link to Learning

Visit this site to learn more about alkaline batteries.

Rechargeable (Secondary) Batteries

Nickel-cadmium, or NiCd, batteries (Figure 16.8.4) consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a "jelly-roll" design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. The reactions are

$$\begin{array}{lll} \text{anode:} & \mathrm{Cd(s) + 2\,OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2\,e^-} & \\ \text{cathode:} & \mathrm{NiO_2(s) + 2\,H_2O(l) + 2\,e^- \longrightarrow Ni(OH)_2(s) + 2\,OH^-(aq)} & \\ \hline \text{cell:} & \mathrm{Cd(s) + NiO_2(s) + 2\,H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)} & E_{\text{cell}} \approx +1.2\,\text{V} \end{array}$$

When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be ruptured or incinerated, and they should be disposed of in accordance with relevant toxic waste guidelines.

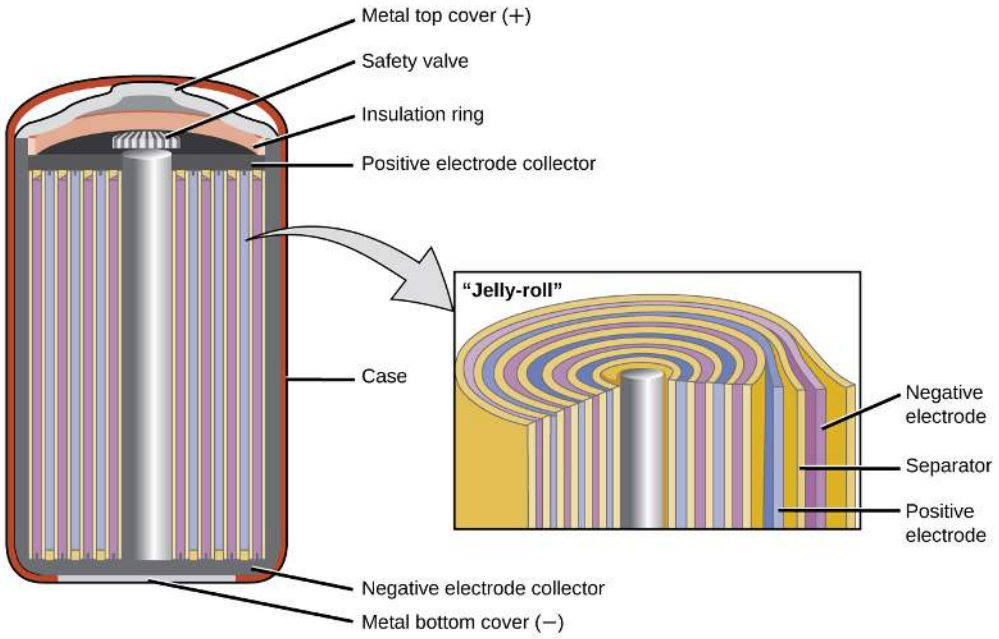


Figure 16.8.4: NiCd batteries use a "jelly-roll" design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.

Link to Learning

Visit this site for more information about nickel cadmium rechargeable batteries.

Lithium ion batteries (Figure 16.8.5) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

$$\begin{array}{lll} \text{anode:} & \mathrm{LiCoO_2 \longrightarrow Li_{1-x}CoO_2 + x\,Li^+ + x\,e^-} & \\ \text{cathode:} & \mathrm{x\,Li^+ + x\,e^- + x\,C_6 \longrightarrow x\,LiC_6} & \\ \hline \text{cell:} & \mathrm{LiCoO_2 + x\,C_6 \longrightarrow Li_{1-x}CoO_2 + x\,LiC_6} & E_{\text{cell}} \approx +3.7\ \text{V} \end{array}$$

The variable stoichiometry of the cell reaction leads to variation in cell voltages, but for typical conditions, *x* is usually no more than 0.5 and the cell voltage is approximately 3.7 V. Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

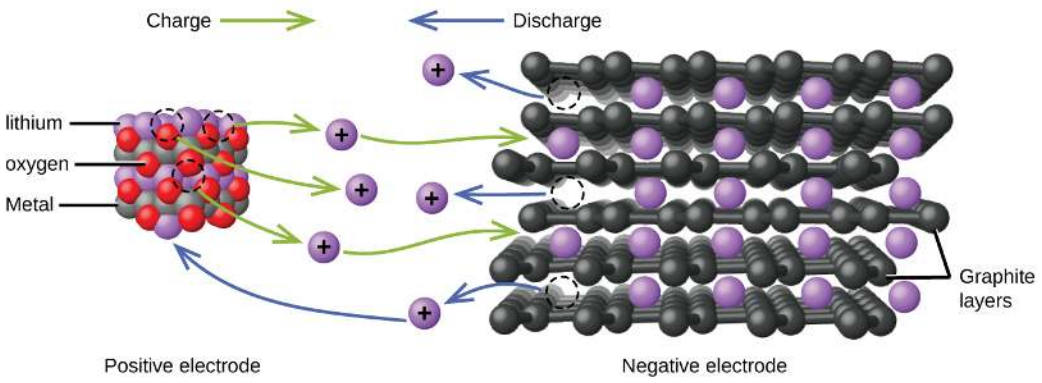


Figure 16.8.5: In a lithium ion battery, charge flows as the lithium ions are transferred between the anode and cathode.

Link to Learning

Visit this site for more information about lithium ion batteries.

The lead acid battery (Figure 16.8.6) is the type of secondary battery commonly used in automobiles. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are

$$\begin{array}{ll} \text{anode:} & \mathrm{Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2\,e^-} \\ \text{cathode:} & \mathrm{PbO_2(s) + HSO_4^-(aq) + 3\,H^+(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)} \\ \hline \text{cell:} & \mathrm{Pb(s) + PbO_2(s) + 2\,H_2SO_4(aq) \longrightarrow 2\,PbSO_4(s) + 2\,H_2O(l)} \qquad E_{\text{cell}} \approx +2\text{ V} \end{array}$$

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, $H_2SO_4(aq)$, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

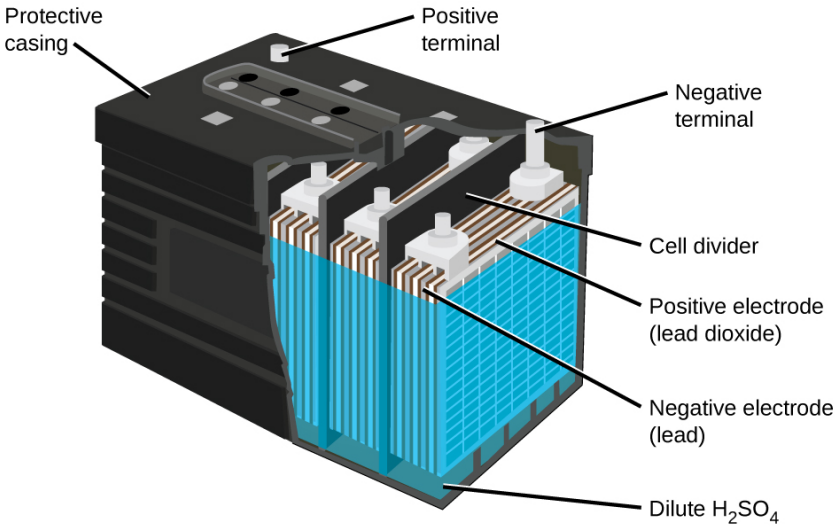


Figure 16.8.6: The lead acid battery in your automobile consists of six cells connected in series to give 12 V.

Link to Learning

Visit this site for more information about lead acid batteries.

Fuel Cells

A fuel cell is a galvanic cell that uses traditional combustive fuels, most often hydrogen or methane, that are continuously fed into the cell along with an oxidant. (An alternative, but not very popular, name for a fuel cell is a *flow battery*.) Within the cell, fuel and oxidant undergo the same redox chemistry as when they are combusted, but via a catalyzed electrochemical that is significantly more efficient. For example, a typical hydrogen fuel cell uses graphite electrodes embedded with platinum-based catalysts to accelerate the two half-cell reactions:

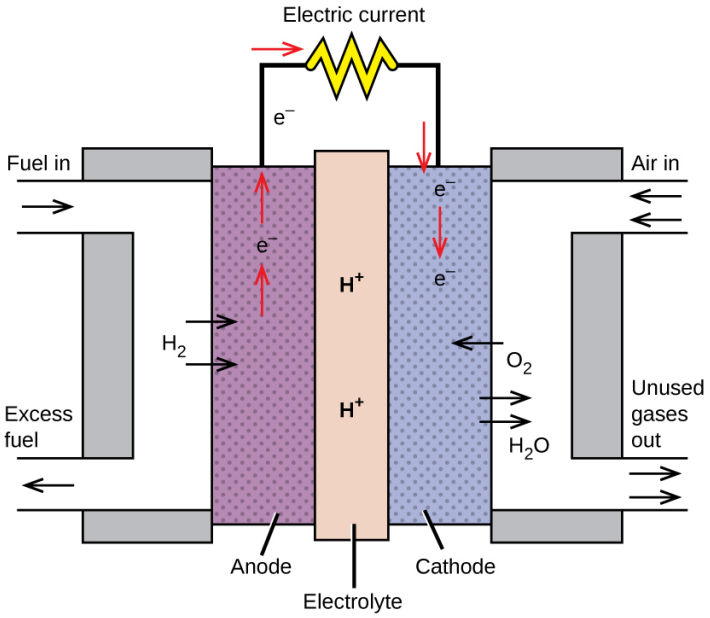


Figure 16.8.7: In this hydrogen fuel cell, oxygen from the air reacts with hydrogen, producing water and electricity.

$$\begin{array}{ll} \text{anode:} & 2\,H_2(g) \longrightarrow 4\,H^+(aq) + 4\,e^- \\ \text{cathode:} & O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(g) \\ \hline \text{cell:} & 2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) \qquad E_{\text{cell}} \approx +1.2\,\text{V} \end{array}$$

These types of fuel cells generally produce voltages of approximately 1.2 V. Compared to an internal combustion engine, the energy efficiency of a fuel cell using the same redox reaction is typically more than double (~20%–25% for an engine versus ~50%–75% for a fuel cell). Hydrogen fuel cells are commonly used on extended space missions, and prototypes for personal vehicles have been developed, though the technology remains relatively immature.

Link to Learning

Check out this link to learn more about fuel cells.

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16.9: Corrosion

Learning Objectives

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

- Define corrosion
- List some of the methods used to prevent or slow corrosion

Corrosion is usually defined as the degradation of metals by a naturally occurring electrochemical process. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper are all examples of corrosion. The total cost of corrosion remediation in the United States is significant, with estimates in excess of half a trillion dollars a year.

Chemistry in Everyday Life: Statue of Liberty: Changing Colors

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green color (Figure 16.9.1). When this statue was first delivered from France, its appearance was not green. It was brown, the color of its copper "skin." So how did the Statue of Liberty change colors? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occur in several steps. Copper metal is oxidized to copper(I) oxide (Cu_2O), which is red, and then to copper(II) oxide, which is black

$$2\,Cu(s) + \tfrac{1}{2}O_2(g) \longrightarrow Cu_2O(s) \qquad \text{(red)}$$

$$2\,Cu_2O(s) + \tfrac{1}{2}O_2(g) \longrightarrow 2\,CuO(s) \qquad \text{(black)}$$

Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, atmospheric sulfur trioxide, carbon dioxide, and water all reacted with the CuO:

$$2\,CuO(s) + CO_2(g) + H_2O(l) \longrightarrow Cu_2CO_3(OH)_2(s) \qquad \text{(green)}$$

$$3\,CuO(s) + 2\,CO_2(g) + H_2O(l) \longrightarrow Cu_2(CO_3)_2(OH)_2(s) \qquad \text{(blue)}$$

$$4\,CuO(s) + SO_3(g) + 3\,H_2O(l) \longrightarrow Cu_4SO_4(OH)_6(s) \qquad \text{(green)}$$

These three compounds are responsible for the characteristic blue-green patina seen on the Statue of Liberty (and other outdoor copper structures). Fortunately, formation of patina creates a protective layer on the copper surface, preventing further corrosion of the underlying copper. The formation of the protective layer is called *passivation*, a phenomenon discussed further in another chapter of this text.



(a) (b)

Figure 16.9.1: (a) The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today.

Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. Rust formation involves the creation of a galvanic cell at an iron surface, as illustrated in Figure 16.9.1. The relevant redox reactions are described by the following equations:

anode:	$\mathrm{Fe(s) \longrightarrow Fe^{2+}(aq) + 2\,e^-}$	$E^\circ_{\mathrm{Fe^{2+}/Fe}} = -0.44\ \mathrm{V}$
cathode:	$\mathrm{O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)}$	$E^\circ_{\mathrm{O_2/O^{2-}}} = +1.23\ \mathrm{V}$
overall:	$\mathrm{2\,Fe(s) + O_2(g) + 4\,H^+(aq) \longrightarrow 2\,Fe^{2+}(aq) + 2\,H_2O(l)}$	$E^\circ_{\mathrm{cell}} = +1.67\ \mathrm{V}$

Further reaction of the iron(II) product in humid air results in the production of an iron(III) oxide hydrate known as rust:

$$\mathrm{4\,Fe^{2+}(aq) + O_2(g) + (4 + 2\,x)\,H_2O(l) \longrightarrow 2\,Fe_2O_3 \cdot x\,H_2O(s) + 8\,H^+(aq)}$$

The stoichiometry of the hydrate varies, as indicated by the use of *x* in the compound formula. Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.

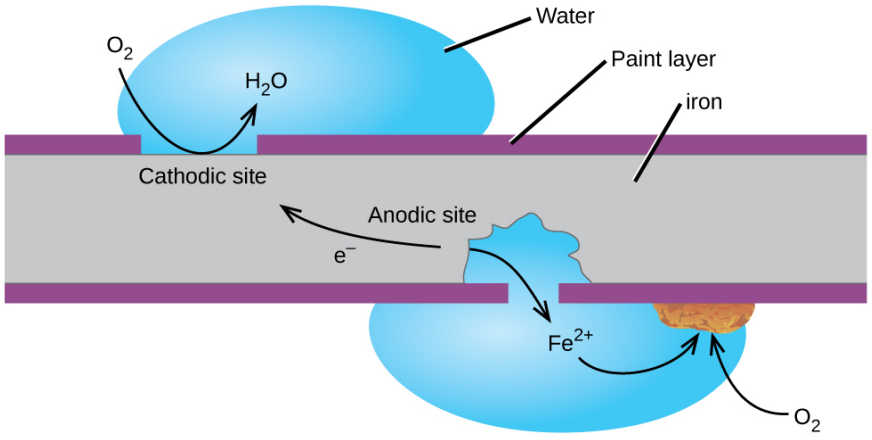


Figure 16.9.2: Corrosion can occur when a painted iron or steel surface is exposed to the environment by a scratch through the paint. A galvanic cell results that may be approximated by the simplified cell schematic Fe(*s*) | $Fe^{2+}(aq)$ ||$O_2(aq)$, $H_2O(l)$ | Fe(*s*).

One way to keep iron from corroding is to keep it painted. The layer of paint prevents the water and oxygen necessary for rust formation from coming into contact with the iron. As long as the paint remains intact, the iron is protected from corrosion.

Other strategies include alloying the iron with other metals. For example, stainless steel is an alloy of iron containing a small amount of chromium. The chromium tends to collect near the surface, where it corrodes and forms a passivating an oxide layer that protects the iron.

Iron and other metals may also be protected from corrosion by **galvanization**, a process in which the metal to be protected is coated with a layer of a more readily oxidized metal, usually zinc. When the zinc layer is intact, it prevents air from contacting the underlying iron and thus prevents corrosion. If the zinc layer is breached by either corrosion or mechanical abrasion, the iron may still be protected from corrosion by a *cathodic protection* process, which is described in the next paragraph.

Another important way to protect metal is to make it the cathode in a galvanic cell. This is **cathodic protection** and can be used for metals other than just iron. For example, the rusting of underground iron storage tanks and pipes can be prevented or greatly reduced by connecting them to a more active metal such as zinc or magnesium (Figure 16.9.3). This is also used to protect the metal parts in water heaters. The more active metals (lower reduction potential) are called **sacrificial anodes** because as they get used up as they corrode (oxidize) at the anode. The metal being protected serves as the cathode for the reduction of oxygen in air, and so it simply serves to conduct (not react with) the electrons being transferred. When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.

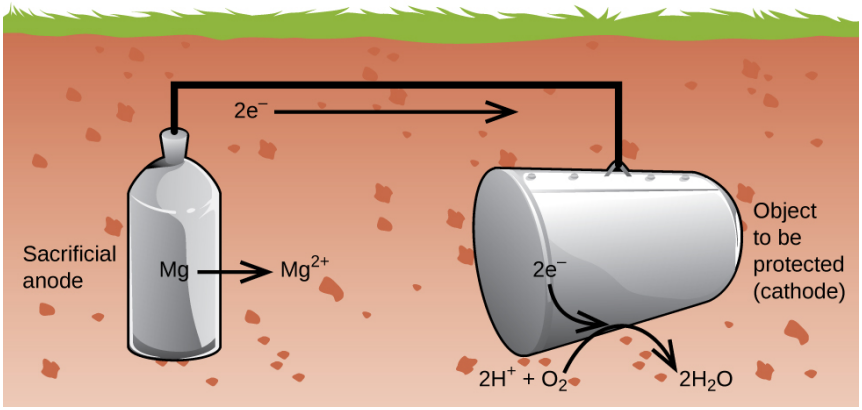


Figure 16.9.3: Cathodic protection is a useful approach to electrochemically preventing corrosion of underground storage tanks.

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16.10: Electrolysis

Learning Objectives

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

- Describe the process of electrolysis
- Compare the operation of electrolytic cells with that of galvanic cells
- Perform stoichiometric calculations for electrolytic processes

Electrochemical cells in which spontaneous redox reactions take place (*galvanic cells*) have been the topic of discussion so far in this chapter. In these cells, *electrical work is done by a redox system on its surroundings* as electrons produced by the redox reaction are transferred through an external circuit. This final section of the chapter will address an alternative scenario in which *an external circuit does work on a redox system* by imposing a voltage sufficient to drive an otherwise nonspontaneous reaction, a process known as **electrolysis**. A familiar example of electrolysis is recharging a battery, which involves use of an external power source to drive the spontaneous (discharge) cell reaction in the reverse direction, restoring to some extent the composition of the half-cells and the voltage of the battery. Perhaps less familiar is the use of electrolysis in the refinement of metallic ores, the manufacture of commodity chemicals, and the *electroplating* of metallic coatings on various products (e.g., jewelry, utensils, auto parts). To illustrate the essential concepts of electrolysis, a few specific processes will be considered.

The Electrolysis of Molten Sodium Chloride

Metallic sodium, Na, and chlorine gas, Cl_2, are used in numerous applications, and their industrial production relies on the large-scale electrolysis of molten sodium chloride, NaCl(*l*). The industrial process typically uses a *Downs cell* similar to the simplified illustration shown in Figure 16.10.1. The reactions associated with this process are:

$$\begin{array}{lll} \text{oxidation:} & 2\,\mathrm{Cl^-(l)} & \longrightarrow \mathrm{Cl_2(g) + 2}e^- \\ + \quad \text{reduction:} & \mathrm{Na^+(l) + e^-} & \longrightarrow \mathrm{Na(l)} \\ \hline \text{cell:} & 2\,\mathrm{Cl^-(l) + 2\,Na^+(l)} & \longrightarrow 2\,\mathrm{Na(l) + Cl_2(g) + 2}e^- \end{array}$$

The cell potential for the above process is negative, indicating the reaction as written (decomposition of liquid NaCl) is not spontaneous. To force this reaction, *a positive potential of magnitude greater than the negative cell potential* must be applied to the cell.

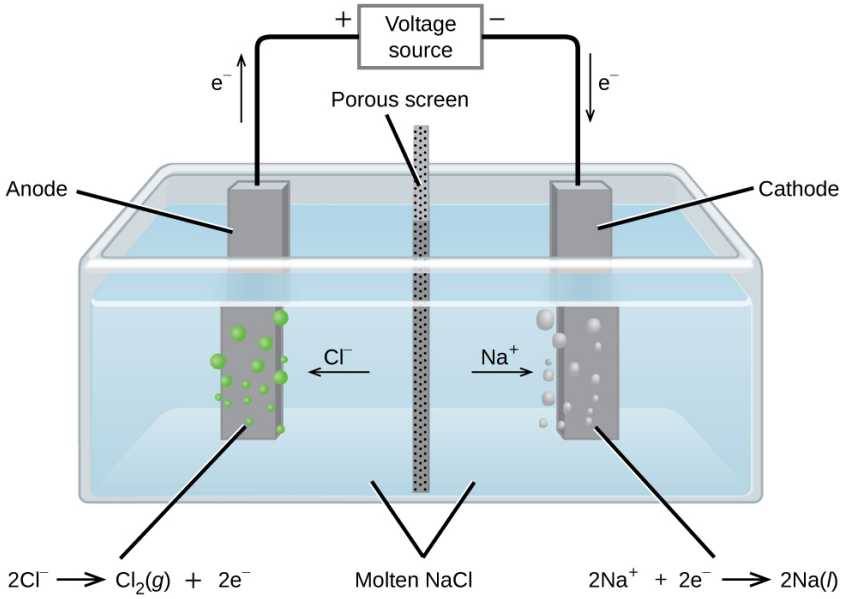


Figure 16.10.1: Cells of this sort (a cell for the electrolysis of molten sodium chloride) are used in the *Downs process* for production of sodium and chlorine, and they typically use iron cathodes and carbon anodes.

The Electrolysis of Water

Water may be electrolytically decomposed in a cell similar to the one illustrated in Figure 16.10.2 To improve electrical conductivity without introducing a different redox species, the hydrogen ion concentration of the water is typically increased by addition of a strong acid. The redox processes associated with this cell are

	oxidation:	$2\,H_2(l)$	$\longrightarrow O_2(g) + 4\,H^+ + 4\,e^-$	$E^o_{anode} = +1.299\ V$
+	reduction:	$2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2(g)$	$E^o_{anode} = 0\ V$
	cell:	$2\,H_2O(l)$	$\longrightarrow 2\,H_2(g) + O_2(g$	$E^o_{cell} = -1.299\ V$

Again, the cell potential as written is negative, indicating a nonspontaneous cell reaction that must be driven by imposing a cell voltage greater than +1.229 V. Keep in mind that *standard* electrode potentials are used to inform thermodynamic predictions here, though the cell is *not* operating under standard state conditions. Therefore, at best, calculated cell potentials should be considered ballpark estimates.

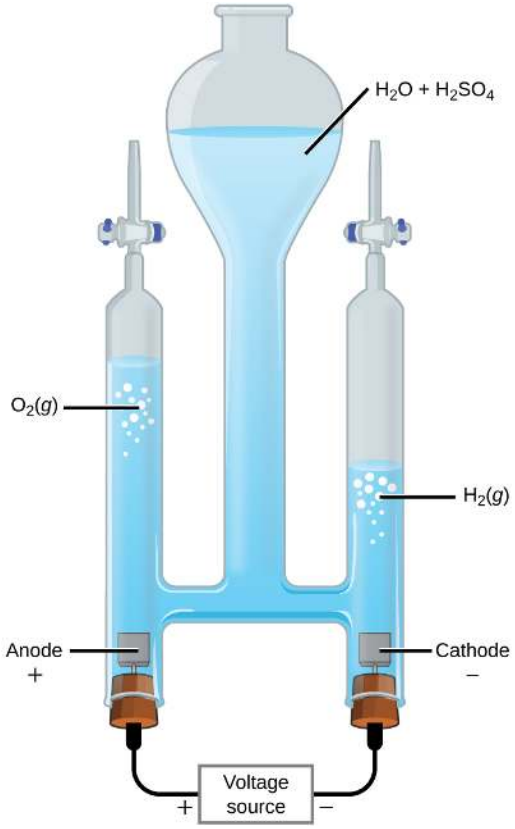


Figure 16.10.2: The electrolysis of water produces stoichiometric amounts of oxygen gas at the anode and hydrogen at the anode.

The Electrolysis of Aqueous Sodium Chloride

When aqueous solutions of ionic compounds are electrolyzed, the anode and cathode half-reactions may involve the electrolysis of either water species (H_2O, H^+, OH^-) or solute species (the cations and anions of the compound). As an example, the electrolysis of aqueous sodium chloride could involve either of these two anode reactions:

$$2\,Cl^-(aq) \longrightarrow Cl_2(g) + 2\,e^- \quad E^\circ_{anode} = +1.35827\ V \tag{i}$$

or

$$2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- \quad E^\circ_{anode} = +1.229\ V \tag{ii}$$

The standard electrode (*reduction*) potentials of these two half-reactions indicate water may be *oxidized* at a less negative/more positive potential (–1.229 V) than chloride ion (–1.358 V). Thermodynamics thus predicts that water would be more readily

oxidized, though in practice it is observed that both water and chloride ion are oxidized under typical conditions, producing a mixture of oxygen and chlorine gas.

Turning attention to the cathode, the possibilities for reduction are:

$$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g) \quad E^\circ_{anode} = 0\,V \tag{iii}$$

or

$$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 4\,OH^-(aq) \quad E^\circ_{anode} = -0.8277\,V \tag{iv}$$

or

$$Na^+(aq) + e^- \longrightarrow Na(s) \quad E^\circ_{anode} = -2.71\,V \tag{v}$$

Comparison of these *standard* half-reaction potentials suggests the reduction of hydrogen ion is thermodynamically favored. However, in a neutral aqueous sodium chloride solution, the concentration of hydrogen ion is far below the standard state value of 1 *M* (approximately 10^{-7} *M*), and so the observed cathode reaction is actually reduction of water. The net cell reaction in this case is then

$$2\,H_2O(l) + 2\,Cl^-(aq) \longrightarrow H_2(g) + Cl_2(g) + 2\,OH^-(aq) \quad E^\circ_{cell} = -2.186\,V$$

This electrolysis reaction is part of the *chlor-alkali process* used by industry to produce chlorine and sodium hydroxide (lye).

Chemistry in Everyday Life: Electroplating

An important use for electrolytic cells is in electroplating. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chrome-plated automobile parts, and jewelry. The silver plating of eating utensils is used here to illustrate the process. (Figure 16.10.3).

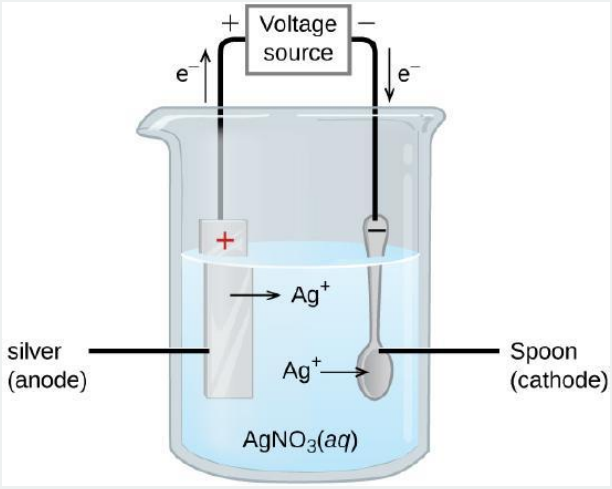


Figure 16.10.3: This schematic shows an electrolytic cell for silver plating eating utensils.

In the figure, the anode consists of a silver electrode, shown on the left. The cathode is located on the right and is the spoon, which is made from inexpensive metal. Both electrodes are immersed in a solution of silver nitrate. Applying a sufficient potential results in the oxidation of the silver anode

$$Ag(s) \longrightarrow Ag^+(aq) + e^- \qquad (anode)$$

and reduction of silver ion at the (spoon) cathode:

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad (cathode)$$

The net result is the transfer of silver metal from the anode to the cathode. Several experimental factors must be carefully controlled to obtain high-quality silver coatings, including the exact composition of the electrolyte solution, the cell voltage applied, and the rate of the electrolysis reaction (electrical current).

Quantitative Aspects of Electrolysis

Electrical current is defined as the rate of flow for any charged species. Most relevant to this discussion is the flow of electrons. Current is measured in a composite unit called an ampere, defined as one coulomb per second (A = 1 C/s). The charge transferred, *Q*, by passage of a constant current, *I*, over a specified time interval, *t*, is then given by the simple mathematical product

$$Q = It$$

When electrons are transferred during a redox process, the stoichiometry of the reaction may be used to derive the total amount of (electronic) charge involved. For example, the generic reduction process

$$\mathrm{M^{n^+}(aq) + n\,e^- \longrightarrow M(s)}$$

involves the transfer of n mole of electrons. The total charge transferred is, therefore,

$$Q = nF$$

where F is Faraday's constant, the charge in coulombs for one mole of electrons. If the reaction takes place in an electrochemical cell, the current flow is conveniently measured, and it may be used to assist in stoichiometric calculations related to the cell reaction.

Example 16.10.1: Converting Current to Moles of Electrons

In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

Solution

Faraday's constant can be used to convert the charge (*Q*) into moles of electrons (*n*). The charge is the current (*I*) multiplied by the time

$$n = \frac{Q}{F} = \frac{\frac{10.23C}{s} \times 1hr \times \frac{60min}{hr} \times \frac{60s}{\text{min}}}{96,485C/mole^-} = \frac{36,830C}{96,485C/mole^-} = 0.3817mole^-$$

From the problem, the solution contains $AgNO_3$, so the reaction at the cathode involves 1 mole of electrons for each mole of silver

$$\mathrm{Ag^+(aq) + e^- \longrightarrow Ag(s)} \qquad \text{(cathode)}$$

The atomic mass of silver is 107.9 g/mol, so

$$\text{mass } Ag = 0.3817 \text{ mol } \mathrm{e^-} \times \frac{1 \text{ mol Ag}}{1 \text{ mol } \mathrm{e^-}} \times \frac{107.9 \text{ g Ag}}{1 \text{ mol Ag}} = 41.19 \text{ g Ag}$$

Exercise 16.10.1

Aluminum metal can be made from aluminum(III) ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of 25.0 A passed through the solution for 15.0 minutes?

Answer

$$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$$

0.0777 mol Al = 2.10 g Al.

Example 16.10.2: Time Required for Deposition

In one application, a 0.010-mm layer of chromium must be deposited on a part with a total surface area of 3.3 m^2 from a solution of containing chromium(III) ions. How long would it take to deposit the layer of chromium if the current was 33.46 A? The density of chromium (metal) is 7.19 g/cm^3.

Solution

First, compute the volume of chromium that must be produced (equal to the product of surface area and thickness):

$$\text{volume } = \left(0.010mm \times \frac{1cm}{10mm}\right) \times \left(3.3m^2 \times \left(\frac{10,000cm^2}{1m^2}\right)\right) = 33cm^3$$

Use the computed volume and the provided density to calculate the molar amount of chromium required:

$$\text{mass } = \text{ volume } \times \text{ density } = 33cm^3 \times \frac{7.19g}{cm^3} = 237gCr$$

$$molCr = 237gCr \times \frac{1molCr}{52.00gCr} = 4.56molCr$$

The stoichiometry of the chromium(III) reduction process requires three moles of electrons for each mole of chromium(0) produced, and so the total charge required is:

$$Q = 4.56molCr \times \frac{3mole^-}{1molCr} \times \frac{96485C}{mole^-} = 1.32 \times 10^6 C$$

Finally, if this charge is passed at a rate of 33.46 C/s, the required time is:

$$t = \frac{Q}{I} = \frac{1.32 \times 10^6 C}{33.46 C/s} = 3.95 \times 10^4 s = 11.0hr$$

Exercise 16.10.2

What mass of zinc is required to galvanize the top of a 3.00 m 5.50 m sheet of iron to a thickness of 0.100 mm of zinc? If the zinc comes from a solution of $Zn(NO_3)_2$ and the current is 25.5 A, how long will it take to galvanize the top of the iron? The density of zinc is 7.140 g/cm^3.

Answer

11.8 kg Zn requires 382 hours.

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16.11: Key Terms

active electrode | electrode that participates as a reactant or product in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

alkaline battery | primary battery similar to a *dry cell* that uses an alkaline (often potassium hydroxide) electrolyte; designed to be an improved replacement for the dry cell, but with more energy storage and less electrolyte leakage than typical dry cell

anode | electrode in an electrochemical cell at which oxidation occurs

battery | single or series of galvanic cells designed for use as a source of electrical power

cathode | electrode in an electrochemical cell at which reduction occurs

cathodic protection | approach to preventing corrosion of a metal object by connecting it to a *sacrificial anode* composed of a more readily oxidized metal

cell notation (schematic) | symbolic representation of the components and reactions in an electrochemical cell

cell potential (E_{cell}) | difference in potential of the cathode and anode half-cells

concentration cell | galvanic cell comprising half-cells of identical composition but for the concentration of one redox reactant or product

corrosion | degradation of metal via a natural electrochemical process

dry cell | primary battery, also called a zinc-carbon battery, based on the spontaneous oxidation of zinc by manganese(IV)

electrode potential (E_X) | the potential of a cell in which the half-cell of interest acts as a cathode when connected to the standard hydrogen electrode

electrolysis | process using electrical energy to cause a nonspontaneous process to occur

electrolytic cell | electrochemical cell in which an external source of electrical power is used to drive an otherwise nonspontaneous process

Faraday's constant (F) | charge on 1 mol of electrons; F = 96,485 C/mol e^-

fuel cell | devices similar to galvanic cells that require a continuous feed of redox reactants; also called a *flow battery*

galvanic (voltaic) cell | electrochemical cell in which a spontaneous redox reaction takes place; also called a *voltaic cell*

galvanization | method of protecting iron or similar metals from corrosion by coating with a thin layer of more easily oxidized zinc.

half cell | component of a cell that contains the redox conjugate pair ("couple") of a single reactant

inert electrode | electrode that conducts electrons to and from the reactants in a half-cell but that is not itself oxidized or reduced

lead acid battery | rechargeable battery commonly used in automobiles; it typically comprises six galvanic cells based on Pb half-reactions in acidic solution

lithium ion battery | widely used rechargeable battery commonly used in portable electronic devices, based on lithium ion transfer between the anode and cathode

Nernst equation | relating the potential of a redox system to its composition

nickel-cadmium battery | rechargeable battery based on Ni/Cd half-cells with applications similar to those of lithium ion batteries

primary cell | nonrechargeable battery, suitable for single use only

sacrificial anode | electrode constructed from an easily oxidized metal, often magnesium or zinc, used to prevent corrosion of metal objects via cathodic protection

salt bridge | tube filled with inert electrolyte solution

secondary cell | battery designed to allow recharging

standard cell potential | the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 *M* for solutes), usually at 298.15 K

standard electrode potential () | electrode potential measured under standard conditions (1 bar or 1 atm for gases; 1 *M* for solutes) usually at 298.15 K

standard hydrogen electrode (SHE) | half-cell based on hydrogen ion production, assigned a potential of exactly 0 V under standard state conditions, used as the universal reference for measuring electrode potential

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16.12: Key Equations

$$\Delta G = -nFE_{\text{cell}}$$

$$Q = I\,t = n\,F$$

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CHAPTER OVERVIEW

17: Bonding in Transition Metal Compounds and Coordination Complexes

17.1: Chemistry of the Transition Metals
17.2: Bonding in Simple Molecules That Contain Transition Metals
17.3: Introduction to Coordination Chemistry
17.4: Structures of Coordination Complexes
17.5: Crystal Field Theory- Optical and Magnetic Properties
17.6: Optical Properties and the Spectrochemical Series
17.7: Bonding in Coordination Complexes

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17.1: Chemistry of the Transition Metals

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

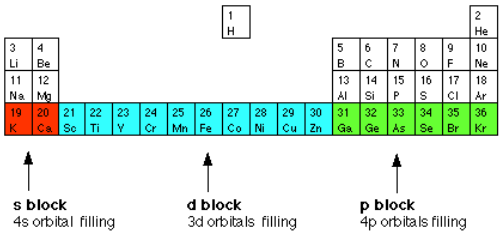
What is a transition metal?

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

d-block elements

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

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



The electronic structures of the d block elements shown are:

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

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

Transition metals

Not all d block elements count as transition metals! There are two slightly different definitions in use at the moment both of which crop up in various uses:

The official IUPAC definition:

A transition metal is one which has an atom with an incompletely filled d orbital or which forms one or more stable ions with incompletely filled d orbitals.

The older definition:

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

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

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

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

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

Transition metal ions

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

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

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

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

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

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

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

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

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

Variable oxidation state (number)

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

Examples of variable oxidation states in the transition metals

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

+2	in Mn^{2+}

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

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

Explaining the variable oxidation states in the transition metals

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

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

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

Thinking about a typical non-transition metal (calcium)

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

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

Thinking about a typical transition metal (iron)

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

Fe		[Ar] $3d^6 4s^2$
Fe^{2+}		[Ar] $3d^6$
Fe^{3+}		[Ar] $3d^5$

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

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

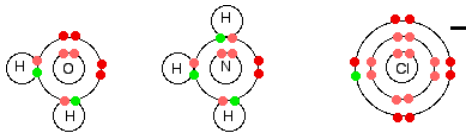
There is an increase in ionization energy as you take more electrons off an atom because you have the same number of protons attracting fewer electrons. However, there is much less increase when you take the third electron from iron than from calcium.

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

The formation of complex ions

What is a complex ion?

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



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

Some examples of complex ions formed by transition metals

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

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

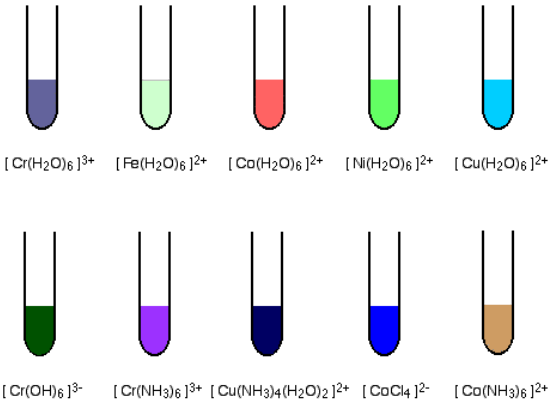
$[Cr(OH)_6]^{3-}$

$[CuCl_4]^{2-}$

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

The formation of colored compounds

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



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

The origin of color in the transition metal ions

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

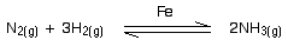
Light is absorbed as electrons move between one d orbital and another. This is explained in detail on another page.

Catalytic Activity

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

Iron in the Haber Process

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



Nickel in the hydrogenation of C=C bonds

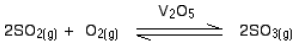
This reaction is at the heart of the manufacture of margarine from vegetable oils. However, the simplest example is the reaction between ethene and hydrogen in the presence of a nickel catalyst.



Transition metal compounds as catalysts

Vanadium(V) oxide in the Contact Process

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



Iron ions in the reaction between persulfate ions and iodide ions

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

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

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- Jim Clark (Chemguide.co.uk)

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17.2: Bonding in Simple Molecules That Contain Transition Metals

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

Introduction

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

Table 17.2.1

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

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

Neutral-Atom Electron Configurations

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

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

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

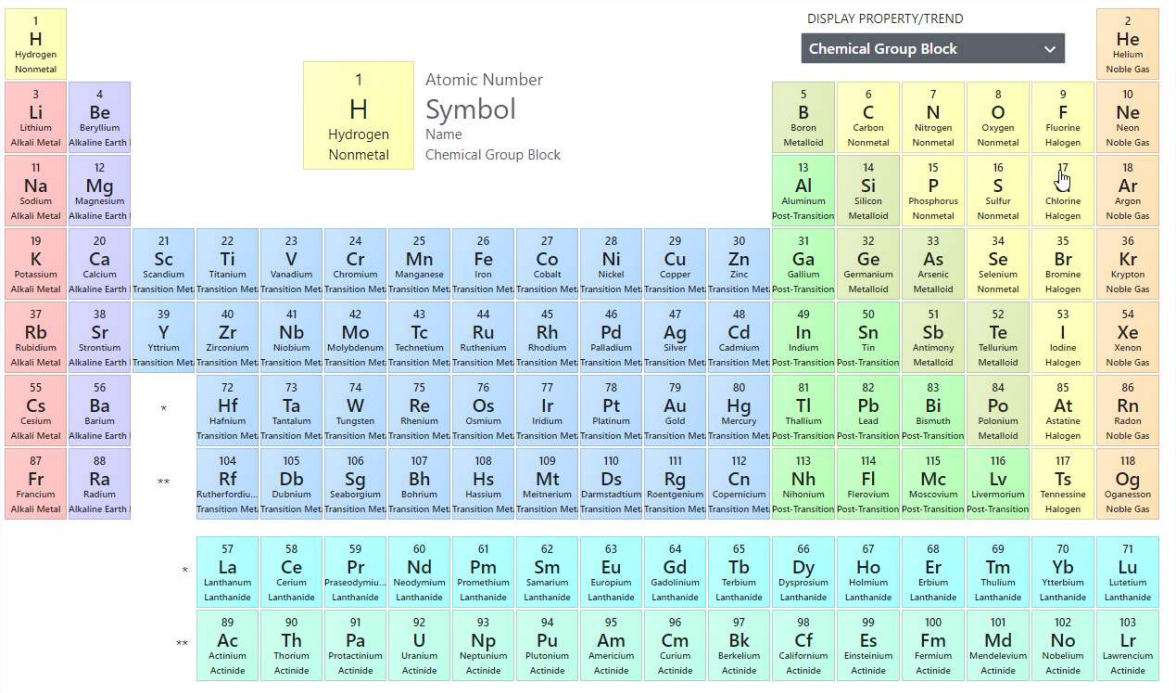


Figure 17.2.1: Periodic Table (Public Domain; PubChem)

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

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

or

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

The neutral atom configurations of the fourth period transition metals are in Table 17.2.2

Table 17.2.2

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

Chromium and copper appear anomalous. Take a brief look at where the element **Chromium** (atomic number 24) lies on the Periodic Table (Figure 17.2.1). The electronic configuration for chromium is not [Ar] $4s^2 3d^4$ but instead it is [Ar] $4s^1 3d^5$. This is because the half-filled 3d manifold (with one 4s electron) is more stable than a partially filled d-manifold (and a filled 4s manifold). You will notice from Table 17.2.2 that the copper exhibits a similar phenomenon, although with a fully filled d-manifold.

Oxidation States of Transition Metal Ions

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

Example 17.2.1

Write the electronic configurations of:

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

Answer

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

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

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

Example 17.2.2

Determine the more stable configuration between the following pair:

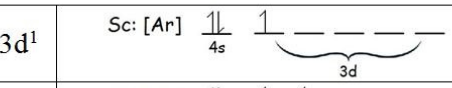
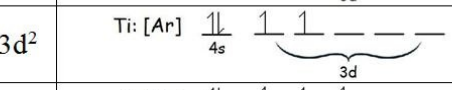
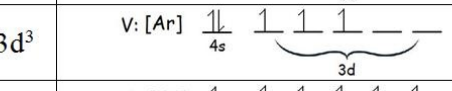
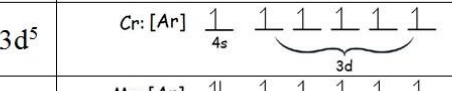
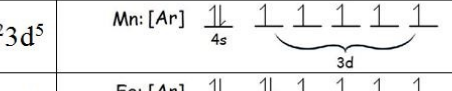
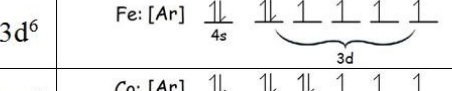
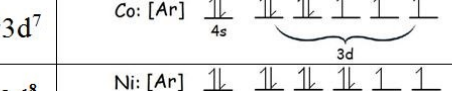
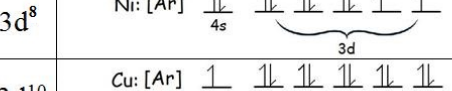
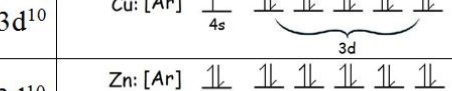
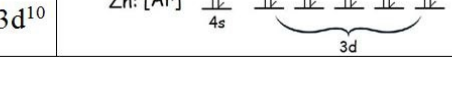
a. [Kr] $5s^2$ $4d^6$ vs. [Kr] $5s^1$ $4d^7$
b. Ag^{1+} vs. Ag^{2+}

Answer

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

Multiple Oxidation States

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

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

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

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

Example 17.2.3

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

Answer

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

Example 17.2.4

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

Answer

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

Example 17.2.5

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

Answer

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

Oxidation State of Transition Metals in Compounds

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

Example 17.2.6

Determine the oxidation state of cobalt in $CoBr_2$.

Answer

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

Example 17.2.7

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

Answer

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

Polyatomic Transition Metal Ions

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

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

Manganese: A Case Study

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



Figure 17.2.2: (left) A rough fragment of lustrous silvery metal (CC BY-SA 3.0; Tomihahndorf via Wikipedia) (right) Some of the Lascaux cave paintings use manganese-based pigments. (Public Domain; Prof saxx via Wikipedia)

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

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

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

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

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

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

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

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

Summary

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

Questions

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

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

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

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

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17.3: Introduction to Coordination Chemistry

Learning Objectives

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

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

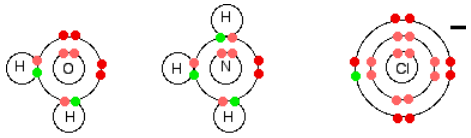


Figure 17.3.1: Simple Bohr diagram bonding in water, ammonia, and the chloride ion.

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

Bonding in Simple Complex Ions

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

Example 17.3.1: $Al(H_2O)_6^{3+}$

Aluminum has the electronic structure

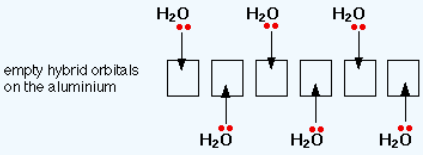
$$1s^2 2s^2 2p^6 3s^2 3p_x^1$$

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

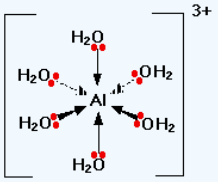
$$1s^2 2s^2 2p^6$$

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

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



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



Because of the movement of electrons towards the center of the ion, the 3+ charge is no longer located entirely on the aluminum, but is now spread over the whole of the ion. Because the aluminum is forming 6 bonds, the co-ordination number of

the aluminum is said to be 6. The co-ordination number of a complex ion counts the number of co-ordinate bonds being formed by the metal ion at its center.

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

Example 17.3.2: $Fe(H_2O)_6^{3+}$

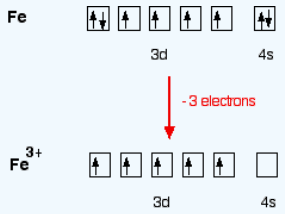
Iron has the electronic structure

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

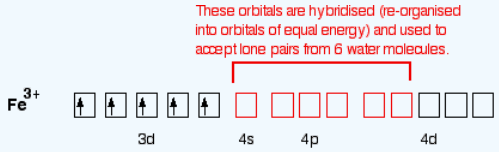
When it forms an Fe^{3+} ion it loses the 4s electrons and one of the 3d electrons to leave

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$$

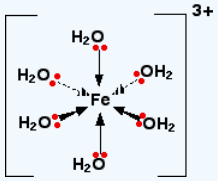
Looking at this as electrons-in-boxes, at the bonding level:



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



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



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

Example 17.3.3: $CuCl_4^{2-}$

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

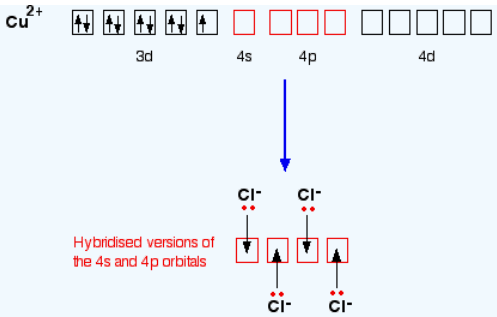
Copper has the electronic structure

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$$

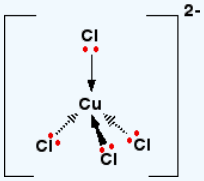
When it forms a Cu^{2+} ion it loses the 4s electron and one of the 3d electrons to leave

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$$

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



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



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

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

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17.4: Structures of Coordination Complexes

Learning Objectives

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

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

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

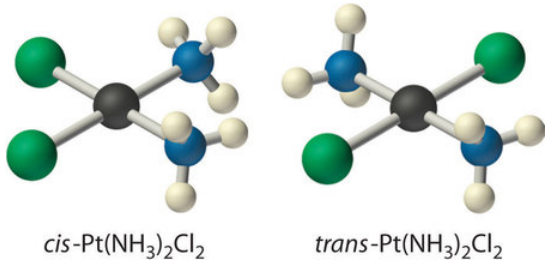


Figure 17.4.1: Two stereoisomers. The atoms are connected to each other in the same order, but differ in their three-dimensional relationships. (left) The cis-Platin compound is square planar at platinum and is flat when viewed from the edge, and square when viewed from the face. (right) The trans-Platin compound is connected in the same way as in cis-platin, and is still square planar, but there is a different 3-dimensional arrangement

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

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

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

CIS/TRANS isomers have different physical properties

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

CIS/TRANS isomers have different biological properties

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

? Exercise 17.4.1

Draw the cis and trans isomers of the following compounds:

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

? Exercise 17.4.2

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

Geometric Isomers

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

Planar Isomers

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

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

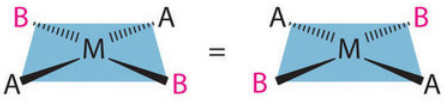


MA_3B square planar complex

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



MA_2B_2 square planar complex, *cis* isomer



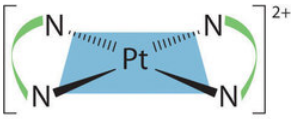
MA_2B_2 square planar complex, *trans* isomer

Figure 17.4.1).

The anticancer drug cisplatin and its inactive trans isomer. Cisplatin is especially effective against tumors of the reproductive organs, which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed

with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin.

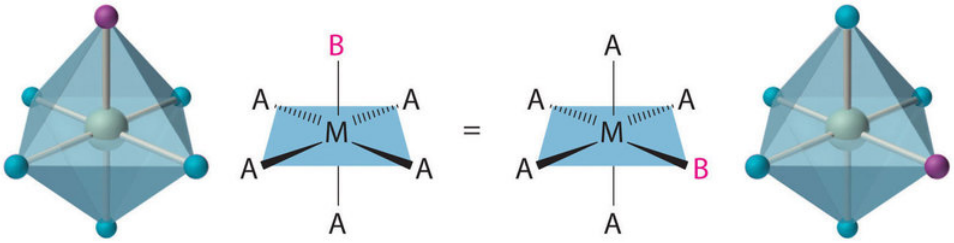
Square planar complexes that contain symmetrical bidentate ligands, such as $[Pt(en)_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:



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

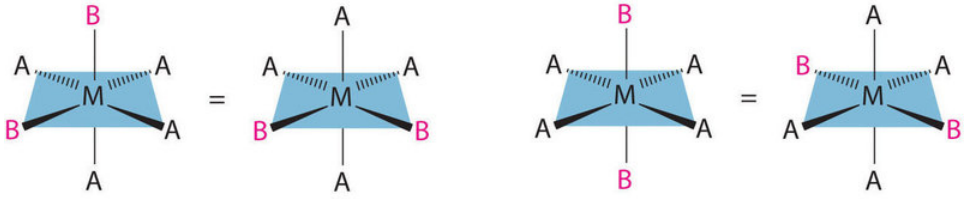
Octahedral Isomers

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



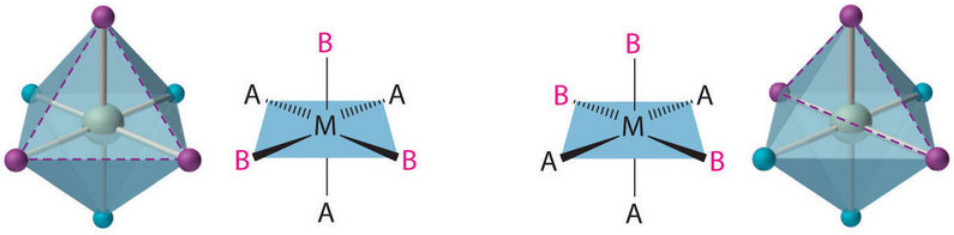
MA_5B octahedral complex

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



MA_4B_2 octahedral complex, *cis* isomer **MA_4B_2 octahedral complex, *trans* isomer**

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



MA_3B_3 octahedral complex, *fac* isomer **MA_3B_3 octahedral complex, *mer* isomer**

Example 17.4.1

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

Given: formula of complex

Asked for: structures of geometrical isomers

Solution

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



H_2O's *trans* **Br, Cl *trans***

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



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

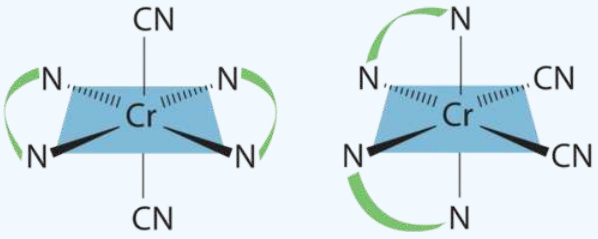
This complex can therefore exist as four different geometrical isomers.

Exercise 17.4.1

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

Answer

Two geometrical isomers are possible: trans and cis.



trans ***cis***

Summary

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

Contributors and Attributions

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17.5: Crystal Field Theory- Optical and Magnetic Properties

Learning Objectives

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

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

d-Orbital Splittings

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

We begin by considering how the energies of the d orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall that the five d orbitals are initially degenerate (have the same energy). If we distribute six negative charges uniformly over the surface of a sphere, the d orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the d orbitals (Figure 17.5.1*a*). Placing the six negative charges at the vertices of an octahedron does not change the average energy of the d orbitals, but it does remove their degeneracy: the five d orbitals split into two groups whose energies depend on their orientations. As shown in Figure 17.5.1*b* the d_{z^2} and $d_{x^2-y^2}$ orbitals point directly at the six negative charges located on the x, y, and z axes. Consequently, the energy of an electron in these two orbitals (collectively labeled the e_g orbitals) will be greater than it will be for a spherical distribution of negative charge because of increased electrostatic repulsions. In contrast, the other three d orbitals (d_{xy}, d_{xz}, and d_{yz}, collectively called the t_{2g} orbitals) are all oriented at a 45° angle to the coordinate axes, so they point between the six negative charges. The energy of an electron in any of these three orbitals is lower than the energy for a spherical distribution of negative charge.

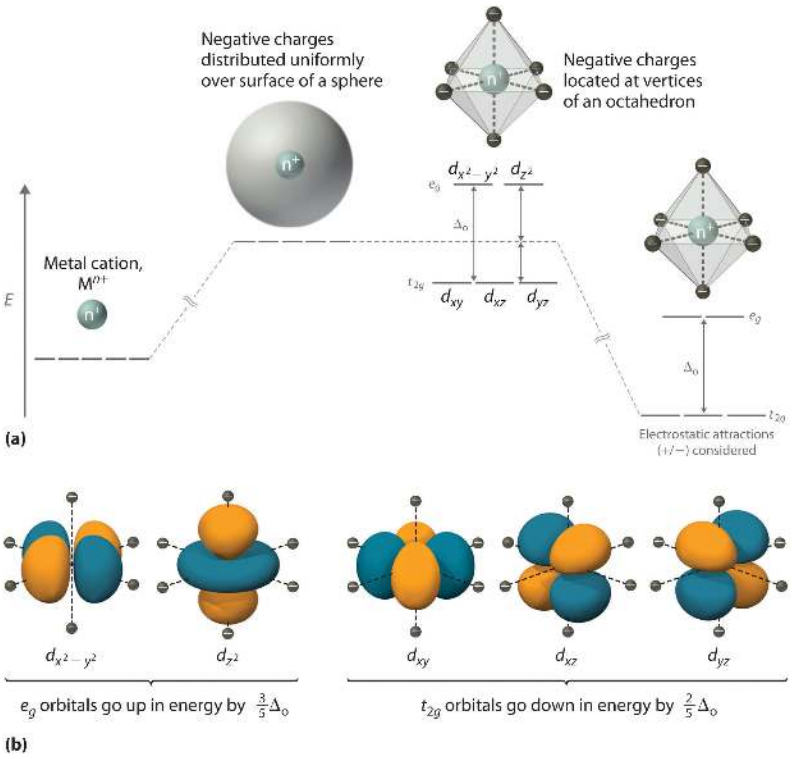


Figure 17.5.1: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies. (a) Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of −1 at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the $d_{x^2-y^2}$ and d_{z^2} orbitals increase in energy, while the, d_{xy}, d_{xz}, and d_{yz} orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a −6 charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. (b) The two e_g orbitals (left) point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of negative charge. In contrast, the three t_{2g} orbitals (right) point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge.

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

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

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

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the d orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the d orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five d orbitals without affecting their splitting (as shown at the far right in Figure 17.5.1*a*).

Electronic Structures of Metal Complexes

We can use the d-orbital energy-level diagram in Figure 17.5.1 to predict electronic structures and some of the properties of transition-metal complexes. We start with the Ti^{3+} ion, which contains a single d electron, and proceed across the first row of the transition metals by adding a single electron at a time. We place additional electrons in the lowest-energy orbital available, while keeping their spins parallel as required by Hund's rule. As shown in Figure 24.6.2, for d^1–d^3 systems—such as $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, and $[Cr(H_2O)_6]^{3+}$, respectively—the electrons successively occupy the three degenerate t_{2g} orbitals with their spins

parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex $[Cr(H_2O)_6]^{3+}$, for example, by saying that the chromium ion has a d^3 electron configuration or, more succinctly, Cr^{3+} is a d^3 ion.

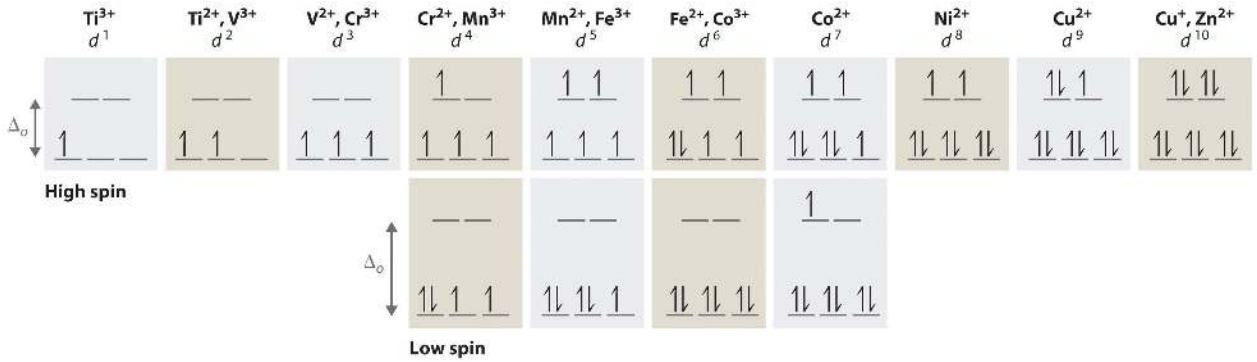


Figure 17.5.2: The Possible Electron Configurations for Octahedral d^n Transition-Metal Complexes (n = 1–10). Two different configurations are possible for octahedral complexes of metals with d^4, d^5, d^6, and d^7 configurations; the magnitude of Δ_o determines which configuration is observed.

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

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

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

Factors That Affect the Magnitude of Δ_o

The magnitude of Δ_o dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ_o (i.e., $\Delta_o > P$) yield a low-spin complex, whereas small values of Δ_o (i.e., $\Delta_o < P$) produce a high-spin complex. As we noted, the magnitude of Δ_o depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of Δ_o for some representative transition-metal complexes are given in Table 17.5.1.

Table 17.5.1: Crystal Field Splitting Energies for Some Octahedral (Δ_o)* and Tetrahedral (Δ_t) Transition-Metal Complexes

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

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

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

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

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

Charge on the Metal Ion

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

Principal Quantum Number of the Metal

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

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

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

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

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

The Nature of the Ligands

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

experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series, shown here in order of decreasing Δ_o:

$$\underset{\text{strong-field ligands}}{\mathrm{CO} \approx \mathrm{CN}^- > \mathrm{NO}_2^-} > \mathrm{en} > \mathrm{NH_3} > \underset{\text{intermediate-field ligands}}{\mathrm{SCN}^- > \mathrm{H_2O} > \mathrm{oxalate}^{2-} > \mathrm{OH}^- > \mathrm{F} > \mathrm{acetate}^-} > \underset{\text{weak-field ligands}}{\mathrm{Cl}^- > \mathrm{Br}^- > \mathrm{I}^-}$$

The values of Δ_o listed in Table 17.5.1 illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

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

Colors of Transition-Metal Complexes

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

Figure 17.5.3: A d–d Transition. In a d–d transition, an electron in one of the t_{2g} orbitals of an octahedral complex such as the $[Cr(H_2O)_6]^{3+}$ ion absorbs a photon of light with energy equal to Δ_o, which causes the electron to move to an empty or singly occupied e_g orbital.

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

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



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

Crystal Field Stabilization Energies

Recall that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of d orbitals (the t_{2g} orbitals) is selectively populated by electrons, then the stability of the complex increases. For example, the single d electron in a d^1 complex such as $[Ti(H_2O)_6]^{3+}$ is located in one of the t_{2g} orbitals. Consequently, this complex will be more stable than expected on purely electrostatic grounds by $0.4\Delta_o$. The additional stabilization of a metal complex by selective population of the lower-energy d orbitals is called its crystal field stabilization energy (CFSE). The CFSE of a complex can be calculated by multiplying the number of electrons in t_{2g} orbitals by the energy of those orbitals ($-0.4\Delta_o$), multiplying the number of electrons in e_g orbitals by the energy of those orbitals ($+0.6\Delta_o$), and summing the two. Table 17.5.2 gives CFSE values for octahedral complexes with different d

electron configurations. The CFSE is highest for low-spin d^6 complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. The other low-spin configurations also have high CFSEs, as does the d^3 configuration.

Table 17.5.2: CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δo)

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

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

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

Example 17.5.1

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

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

Given: complexes

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

Strategy:

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

Solution

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

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

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

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

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

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

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

? Exercise 17.5.1

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

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

Answers

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

Summary

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

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17.6: Optical Properties and the Spectrochemical Series

Learning Objectives

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

Electromagnetic radiation is a form of energy that is produced by oscillating electric and magnetic disturbance, or by the movement of electrically charged particles traveling through a vacuum or matter. Electron radiation is released as photons, which are bundles of light energy that travel at the speed of light as quantized harmonic waves. This energy is then grouped into categories based on its wavelength into the electromagnetic spectrum and have certain characteristics, including amplitude, wavelength, and frequency (Figure 17.6.1).

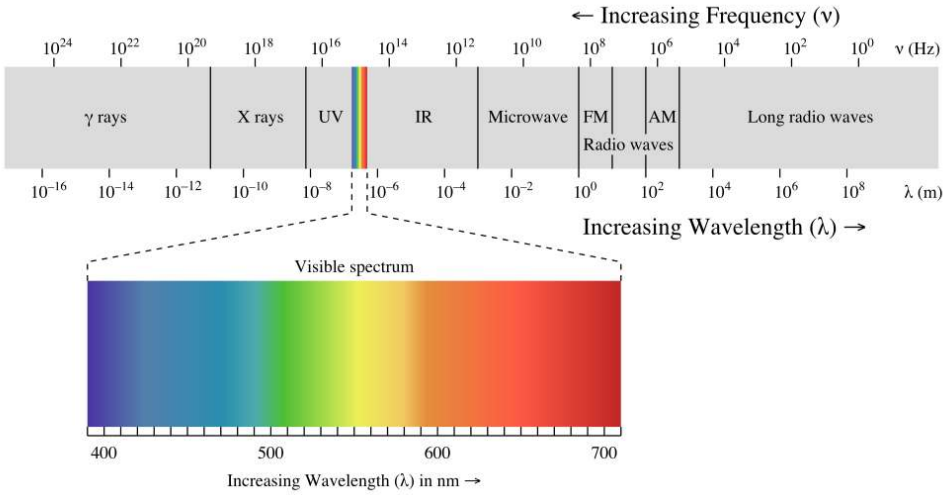


Figure 17.6.1: Electromagnetic spectrum with light highlighted. (CC -SA-BY 2.0 unported; Philip Ronan).

General properties of all electromagnetic radiation include:

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

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

$$E = hu \tag{17.6.1}$$

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

$$E = hu = \frac{hc}{\lambda} \tag{17.6.2}$$

If white light is passed through a prism, it splits into all the colors of the rainbow (Figure 17.6.2). Visible light is simply a small part of an electromagnetic spectrum most of which we cannot see - gamma rays, X-rays, infra-red, radio waves and so on. Each of these has a particular wavelength, ranging from 10^{-16} meters for gamma rays to several hundred meters for radio waves. Visible light has wavelengths from about 400 to 750 nm (1 nanometer = 10^{-9} meters).

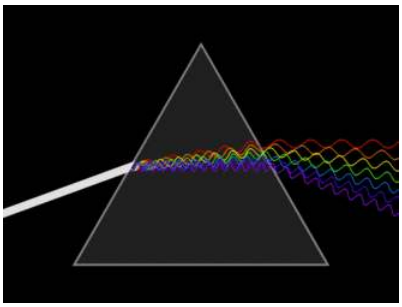
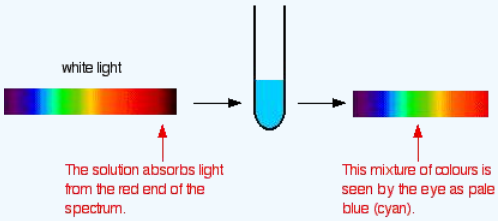


Figure 17.6.2: A triangular prism, dispersing light; waves shown to illustrate the differing wavelengths of light. (Public Domain; Lucas V. Barbosa).

Example 17.6.1: Blue Color of Copper (II) Sulfate in Solution

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



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

Origin of Colors

The process of absorption involves the excitation of the valence electrons in the molecule typically from the low lying level called the Highest Occupied Molecular Orbital (HOMO) into a higher lying state called the the Lowest Unoccupied Molecular Orbital (**LUMO**). When this HOMO and LUMO transition (Figure 17.6.3) involves the absorption of visible light, the sample is colored.

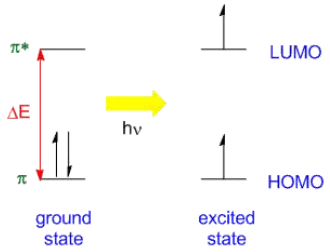


Figure 17.6.4: The general electron excitation process from a HOMO to a LUMO.

The HOMO-LUMO energy difference

$$\Delta E = E_{HOMO} - E_{LUMO} \tag{17.6.3}$$

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

$$\Delta E = hu = \frac{hc}{\lambda} \tag{17.6.4}$$

> *Equation 17.6.4 is the most important equation in the field of light-matter interactions (spectroscopy).*

As Example 17.6.1 demonstrated, when white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown below. Here, complementary colors are diametrically opposite each other (Figure 17.6.5). Thus, absorption of 420-430 nm light renders a substance yellow, and absorption of 500-520 nm light makes it red. Green is unique in that it can be created by absorption close to 400 nm as well as absorption near 800 nm.

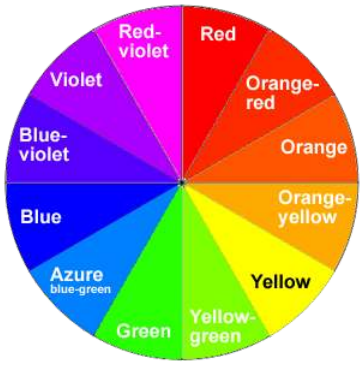


Figure 17.6.5: The color wheel used to identify the color of species.

Colors directly opposite each other on the color wheel are said to be complementary colors. Blue and yellow are complementary colors; red and cyan are complementary; and so are green and magenta. Mixing together two complementary colors of light will give you white light. What this all means is that if a particular color is absorbed from white light, what your eye detects by mixing up all the other wavelengths of light is its complementary color. Copper(II) sulfate solution is pale blue (cyan) because it absorbs light in the red region of the spectrum and cyan is the complementary color of red (Table 17.6.1).

Table 17.6.1: The Visible Spectrum

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

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

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

The Origin of Color in Complex Ions

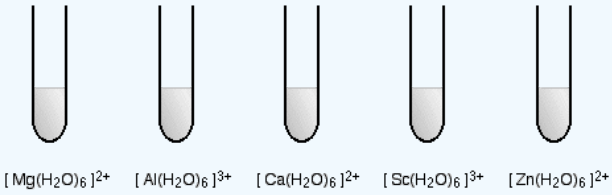
We often casually talk about the transition metals as being those in the middle of the Periodic Table where d orbitals are being filled, but these should really be called d block elements rather than transition elements (or metals). The definition of a transition metal is one which forms one or more stable ions which have incompletely filled d orbitals. Zinc with the electronic structure [Ar] $3d^{10}4s^2$ does not count as a transition metal whichever definition you use. In the metal, it has a full 3d level. When it forms an ion, the 4s electrons are lost - again leaving a completely full 3d level. At the other end of the row, scandium ([Ar] $3d^14s^2$) does not

really counts as a transition metal either. Although there is a partially filled d level in the metal, when it forms its ion, it loses all three outer electrons. The Sc^{3+} ion does not count as a transition metal ion because its 3d level is empty.

Example 17.6.3: Hexaaqua Metal Ions

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

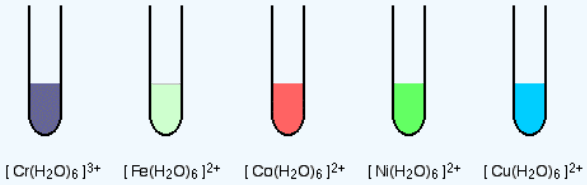
- Non-transition metal ions



These ions are all colorless.

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

- Transition metal ions



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

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

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

Magnetism

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

Paramagnetism

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



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

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

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

Diamagnetism

Diamagnetic substances are characterized by paired electrons—except in the previously-discussed case of transition metals, there are no unpaired electrons. According to the Pauli Exclusion Principle which states that no two identical electrons may take up the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out; thus there is no net magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure 17.6.6

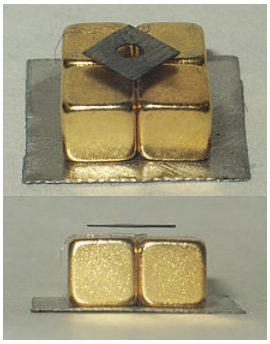


Figure 17.6.6 Levitating pyrolytic carbon: A small (~6 mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5 mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). from Wikipedia.

How to Tell if a Substance is Paramagnetic or Diamagnetic

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

1. Find the electron configuration

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

Example 17.6.4: Chlorine atoms

Are chlorine atoms paramagnetic or diamagnetic?

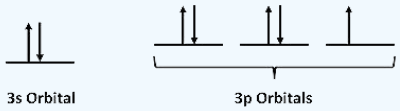
Solution

Step 1: Find the electron configuration

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

Step 2: Draw the valence orbitals

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



Step 3: Look for unpaired electrons

There is one unpaired electron.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

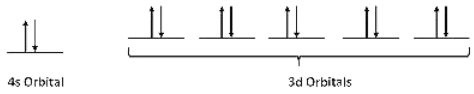
Since there is an unpaired electron, Cl atoms are paramagnetic (but is quite weak).

Example 2: Zinc Atoms

Step 1: Find the electron configuration

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

Step 2: Draw the valence orbitals



Step 3: Look for unpaired electrons

There are no unpaired electrons.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

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

References

1. Pettrucci, Ralph H. General Chemistry: Principles and Modern Applications. 9th. Upper Saddle River: Pearson Prentice Hall, 2007
2. Sherman, Alan, Sharon J. Sherman, and Leonard Russikoff. Basic Concepts of Chemistry Fifth Edition. Boston, MA: Houghton Mifflin Company, 1992. Print.

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17.7: Bonding in Coordination Complexes

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



Figure 17.7.1: The hypothetical "lobster ligand" binds to the Ni^{2+} via two donor sites.

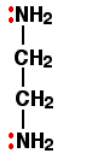
Bidentate binding allows a ligand to bind more tightly. Tridentate ligands, which bind through three donors, can bind even more tightly, and so on. This phenomenon is generally called the "**chelate effect**." This term comes from the Greek chelos, meaning "crab." A crab does not have any teeth at all,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

Complex metal ions containing more complicated ligands

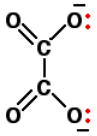
In the examples previously disccussed, each ligand only forms one bond with the central metal ion to give the complex ion. Such a ligand is said to be unidentate. That means literally that it only has one tooth! It only has one pair of electrons that it can use to bond to the metal - any other lone pairs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

Bidentate ligands

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

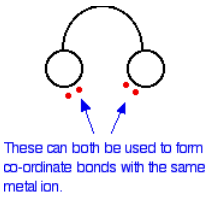


1,2-diaminoethane



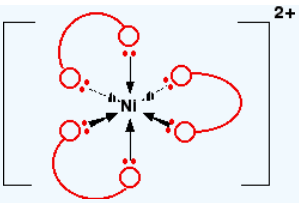
ethanedioate ion

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



Example 17.7.1: $Ni(NH_2CH_2CH_2NH_2)_3^{2+}$

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



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

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

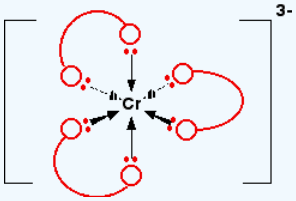
Because the nickel is forming 6 co-ordinate bonds, the coordination number of this ion is 6, despite the fact that it is only joined to 3 ligands. Coordination number counts the number of bonds, not the number of ligands.

Example 5: $Cr(C_2O_4)_3^{3-}$

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

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

The structure of the ion looks like this:

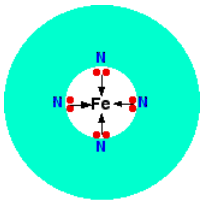


Again, if you drew this in an exam, you would want to show all the atoms properly. If you need to be able to do this, practice drawing it so that it looks clear and tidy! Refer back to the diagram of the ethanedioate ion further up the page to help you.

A Quadridentate Ligand

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

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



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

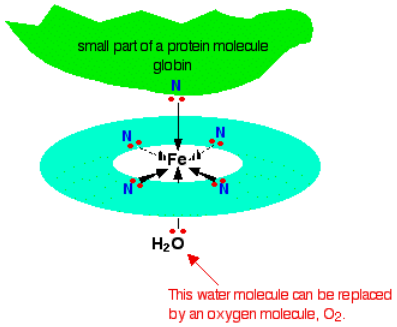


Figure 17.7.2: Overall, the complex ion has a co-ordination number of 6 because the central metal ion is forming 6 co-ordinate bonds.

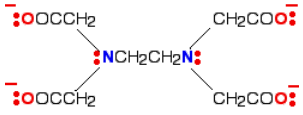
The water molecule which is bonded to the bottom position in the diagram is easily replaced by an oxygen molecule (again via a lone pair on one of the oxygens in O_2) - and this is how oxygen gets carried around the blood by the haemoglobin. When the oxygen gets to where it is needed, it breaks away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

Carbon Monoxide Poisoning

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

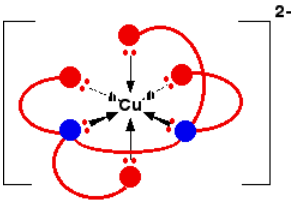
A Hexadentate Ligand

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



the $EDTA^{4-}$ ion

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



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

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

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CHAPTER OVERVIEW

18: Nuclear Chemistry

The chemical reactions that we have considered in previous chapters involve changes in the *electronic* structure of the species involved, that is, the arrangement of the **electrons** around atoms, ions, or molecules. *Nuclear* structure, the numbers of protons and neutrons within the nuclei of the atoms involved, remains unchanged during chemical reactions. This chapter will introduce the topic of nuclear chemistry, which began with the discovery of radioactivity in 1896 by French physicist Antoine Becquerel and has become increasingly important during the twentieth and twenty-first centuries, providing the basis for various technologies related to energy, medicine, geology, and many other areas.

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18.2: Exercises
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18.4: Nuclear Equations
18.5: Radioactive Decay
18.6: Transmutation and Nuclear Energy
18.7: Uses of Radioisotopes
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18.1: Introduction

The chemical reactions that we have considered in previous chapters involve changes in the *electronic* structure of the species involved, that is, the arrangement of the electrons around atoms, ions, or molecules. *Nuclear* structure, the numbers of protons and neutrons within the nuclei of the atoms involved, remains unchanged during chemical reactions.

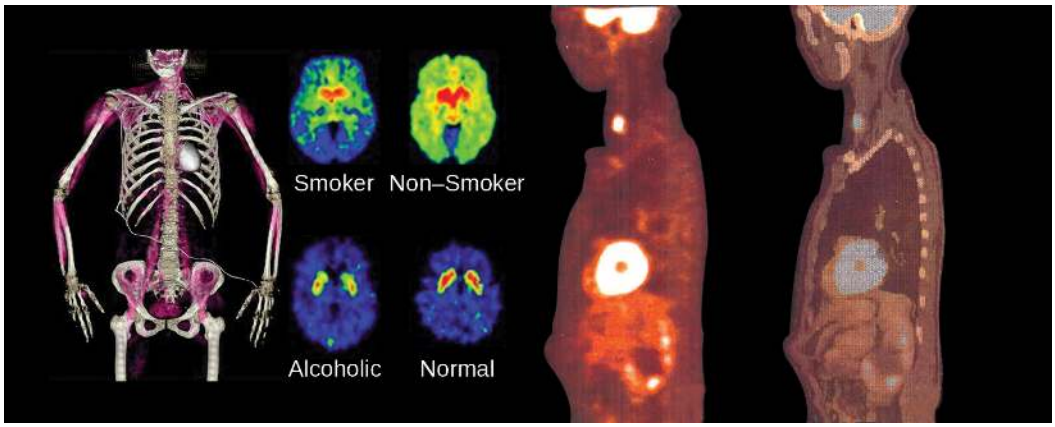


Figure 18.1.1: Nuclear chemistry provides the basis for many useful diagnostic and therapeutic methods in medicine, such as these positron emission tomography (PET) scans. The PET/computed tomography scan on the left shows muscle activity. The brain scans in the center show chemical differences in dopamine signaling in the brains of addicts and nonaddicts. The images on the right show an oncological application of PET scans to identify lymph node metastasis.

This chapter will introduce the topic of nuclear chemistry, which began with the discovery of radioactivity in 1896 by French physicist Antoine Becquerel and has become increasingly important during the twentieth and twenty-first centuries, providing the basis for various technologies related to energy, medicine, geology, and many other areas.

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18.2: Exercises

1. Write the following isotopes in hyphenated form (e.g., “carbon-14”)

(a) $^{24}_{11}\text{Na}$
(b) $^{29}_{13}\text{Al}$
(c) $^{73}_{36}\text{Kr}$
(d) $^{194}_{77}\text{Ir}$

2. Write the following isotopes in nuclide notation (e.g.,

a. oxygen-14
b. copper-70
c. tantalum-175
d. francium-217

3. For the following isotopes that have missing information, fill in the missing information to complete the notation

(a) $^{34}_{14}\text{X}$
(b) $^{36}_{\text{X}}\text{P}$
(c) $^{57}_{\text{X}}\text{Mn}$
(d) $^{121}_{56}\text{X}$

4. For each of the isotopes in Exercise 21.1, determine the numbers of protons, neutrons, and electrons in a neutral atom of the isotope.

5. Write the nuclide notation, including charge if applicable, for atoms with the following characteristics:

a. 25 protons, 20 neutrons, 24 electrons
b. 45 protons, 24 neutrons, 43 electrons
c. 53 protons, 89 neutrons, 54 electrons
d. 97 protons, 146 neutrons, 97 electrons

6. Calculate the density of the nucleus in g/mL, assuming that it has the typical nuclear diameter of 1 10^{-13} cm and is spherical in shape. 7. What are the two principal differences between nuclear reactions and ordinary chemical changes?

8. The mass of the atom is 22.9898 amu.

a. Calculate its binding energy per atom in millions of electron volts.
b. Calculate its binding energy per nucleon.

9. Which of the following nuclei lie within the band of stability shown in Figure 21.2?

a. chlorine-37
b. calcium-40
c. ^{204}Bi
d. ^{56}Fe
e. ^{206}Pb
f. ^{211}Pb
g. ^{222}Rn
h. carbon-14

10. Which of the following nuclei lie within the band of stability shown in Figure 21.2?

a. argon-40
b. oxygen-16
c. ^{122}Ba
d. ^{58}Ni
e. ^{205}Tl
f. ^{210}Tl
g. ^{226}Ra

h. magnesium-24

11. Write a brief description or definition of each of the following:

a. nucleon
b. α particle
c. β particle
d. positron
e. γ ray
f. nuclide
g. mass number
h. atomic number

12. Which of the various particles (α particles, β particles, and so on) that may be produced in a nuclear reaction are actually nuclei?

13. Complete each of the following equations by adding the missing species:

(a) $^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} \rightarrow \ ? + {}^{1}_{0}\mathrm{n}$
(b) $^{239}_{94}\mathrm{Pu} + ? \rightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$
(c) $^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \rightarrow ? + {}^{1}_{1}\mathrm{H}$
(d) $^{235}_{92}\mathrm{U} \rightarrow ? + {}^{135}_{55}\mathrm{Cs} + 4{}^{1}_{0}\mathrm{n}$

14. Complete each of the following equations:

(a) $^{7}_{3}\mathrm{Li} + ? \rightarrow 2{}^{4}_{2}\mathrm{He}$
(b) $^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + \ ?$
(c) $^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} \rightarrow ? + {}^{1}_{0}\mathrm{n}$
(d) $^{250}_{96}\mathrm{Cm} \rightarrow ? + {}^{98}_{38}\mathrm{Sr} + 4{}^{1}_{0}\mathrm{n}$

15. Write a balanced equation for each of the following nuclear reactions:

a. the production of ^{17}O from ^{14}N by α particle bombardment
b. the production of ^{14}C from ^{14}N by neutron bombardment
c. the production of ^{233}Th from ^{232}Th by neutron bombardment
d. the production of ^{239}U from ^{238}U by bombardment

16. Technetium-99 is prepared from ^{98}Mo. Molybdenum-98 combines with a neutron to give molybdenum-99, an unstable isotope that emits a β particle to yield an excited form of technetium-99, represented as ^{99}Tc*. This excited nucleus relaxes to the ground state, represented as ^{99}Tc, by emitting a γ ray. The ground state of ^{99}Tc then emits a β particle. Write the equations for each of these nuclear reactions.

17. The mass of the atom is 18.99840 amu.

a. Calculate its binding energy per atom in millions of electron volts.
b. Calculate its binding energy per nucleon.

18. For the reaction if 100.0 g of carbon reacts, what volume of nitrogen gas (N_2) is produced at 273K and 1 atm?

19. What are the types of radiation emitted by the nuclei of radioactive elements?

20. What changes occur to the atomic number and mass of a nucleus during each of the following decay scenarios?

a. an α particle is emitted
b. a β particle is emitted
c. γ radiation is emitted
d. a positron is emitted
e. an electron is captured

21. What is the change in the nucleus that results from the following decay scenarios?

a. emission of a β particle
b. emission of a β^{+} particle
c. capture of an electron

22. Many nuclides with atomic numbers greater than 83 decay by processes such as electron emission. Explain the observation that the emissions from these unstable nuclides also normally include α particles.

23. Why is electron capture accompanied by the emission of an X-ray?

24. Explain, in terms of Figure 21.2, how unstable heavy nuclides (atomic number > 83) may decompose to form nuclides of greater stability (a) if they are below the band of stability and (b) if they are above the band of stability.

25. Which of the following nuclei is most likely to decay by positron emission? Explain your choice.

a. chromium-53
b. manganese-51
c. iron-59

26. The following nuclei do not lie in the band of stability. How would they be expected to decay? Explain your answer.

(a) $^{34}_{15}\mathrm{P}$
(b) $^{239}_{92}U$
(c) $^{38}_{20}\mathrm{Ca}$
(d) $^{3}_{1}\mathrm{H}$
(e) $^{245}_{94}\mathrm{Pu}$

27. The following nuclei do not lie in the band of stability. How would they be expected to decay?

(a) $^{28}_{15}\mathrm{P}$
(b) $^{235}_{92}\mathrm{U}$
(c) $^{37}_{20}\mathrm{Ca}$
(d) $^{9}_{3}\mathrm{Li}$
(e) $^{245}_{96}\mathrm{Cm}$

28. Predict by what mode(s) of spontaneous radioactive decay each of the following unstable isotopes might proceed:

(a) $^{6}_{2}\mathrm{He}$
(b) $^{60}_{30}\mathrm{Zn}$
(c) $^{235}_{91}\ \mathrm{Pa}$
(d) $^{241}_{94}\ \mathrm{Np}$
(e) $^{18}\ \mathrm{F}$
(f) $^{129}\mathrm{Ba}$
(g) $^{237}\mathrm{Pu}$

29. Write a nuclear reaction for each step in the formation of from which proceeds by a series of decay reactions involving the step-wise emission of α, β, β, α, α, α particles, in that order.

30. Write a nuclear reaction for each step in the formation of from which proceeds by a series of decay reactions involving the step-wise emission of α, α, α, α, β, β, α particles, in that order.

31. Define the term half-life and illustrate it with an example.

32. A 1.00 10^{-6}-g sample of nobelium, has a half-life of 55 seconds after it is formed. What is the percentage of remaining at the following times?

a. 5.0 min after it forms
b. 1.0 h after it forms

33. ^{239}Pu is a nuclear waste byproduct with a half-life of 24,000 y. What fraction of the ^{239}Pu present today will be present in 1000 y?

34. The isotope ^{208}Tl undergoes β decay with a half-life of 3.1 min.

a. What isotope is produced by the decay?
b. How long will it take for 99.0% of a sample of pure ^{208}Tl to decay?
c. What percentage of a sample of pure ^{208}Tl remains un-decayed after 1.0 h?

35. If 1.000 g of produces 0.0001 mL of the gas at STP (standard temperature and pressure) in 24 h, what is the half-life of ^{226}Ra in years?

36. The isotope is one of the extremely hazardous species in the residues from nuclear power generation. The strontium in a 0.500-g sample diminishes to 0.393 g in 10.0 y. Calculate the half-life.

37. Technetium-99 is often used for assessing heart, liver, and lung damage because certain technetium compounds are absorbed by damaged tissues. It has a half-life of 6.0 h. Calculate the rate constant for the decay of

38. What is the age of mummified primate skin that contains 8.25% of the original quantity of ^{14}C?

39. A sample of rock was found to contain 8.23 mg of rubidium-87 and 0.47 mg of strontium-87.

a. Calculate the age of the rock if the half-life of the decay of rubidium by β emission is $4.7\ 10^{10}$ y.
b. If some was initially present in the rock, would the rock be younger, older, or the same age as the age calculated in (a)? Explain your answer.

40. A laboratory investigation shows that a sample of uranium ore contains 5.37 mg of and 2.52 mg of Calculate the age of the ore. The half-life of is $4.5\ 10^{9}$ yr.

41. Plutonium was detected in trace amounts in natural uranium deposits by Glenn Seaborg and his associates in 1941. They proposed that the source of this ^{239}Pu was the capture of neutrons by ^{238}U nuclei. Why is this plutonium not likely to have been trapped at the time the solar system formed $4.7\ 10^{9}$ years ago?

42. A atom (mass = 7.0169 amu) decays into a atom (mass = 7.0160 amu) by electron capture. How much energy (in millions of electron volts, MeV) is produced by this reaction?

43. A atom (mass = 8.0246 amu) decays into a atom (mass = 8.0053 amu) by loss of a β^+ particle (mass = 0.00055 amu) or by electron capture. How much energy (in millions of electron volts) is produced by this reaction?

44. Isotopes such as ^{26}Al (half-life: $7.2\ 10^{5}$ years) are believed to have been present in our solar system as it formed, but have since decayed and are now called extinct nuclides.

a. ^{26}Al decays by β^+ emission or electron capture. Write the equations for these two nuclear transformations.
b. The earth was formed about $4.7\ 10^{9}$ (4.7 billion) years ago. How old was the earth when 99.999999% of the ^{26}Al originally present had decayed?

45. Write a balanced equation for each of the following nuclear reactions:

a. bismuth-212 decays into polonium-212
b. beryllium-8 and a positron are produced by the decay of an unstable nucleus
c. neptunium-239 forms from the reaction of uranium-238 with a neutron and then spontaneously converts into plutonium-239
d. strontium-90 decays into yttrium-90

46. Write a balanced equation for each of the following nuclear reactions:

a. mercury-180 decays into platinum-176
b. zirconium-90 and an electron are produced by the decay of an unstable nucleus
c. thorium-232 decays and produces an alpha particle and a radium-228 nucleus, which decays into actinium-228 by beta decay
d. neon-19 decays into fluorine-19

47. Write the balanced nuclear equation for the production of the following transuranium elements:

a. berkelium-244, made by the reaction of Am-241 and He-4
b. fermium-254, made by the reaction of Pu-239 with a large number of neutrons
c. lawrencium-257, made by the reaction of Cf-250 and B-11
d. dubnium-260, made by the reaction of Cf-249 and N-15

48. How does nuclear fission differ from nuclear fusion? Why are both of these processes exothermic?

49. Both fusion and fission are nuclear reactions. Why is a very high temperature required for fusion, but not for fission?

50.Cite the conditions necessary for a nuclear chain reaction to take place. Explain how it can be controlled to produce energy, but not produce an explosion.

51. Describe the components of a nuclear reactor.

52. In usual practice, both a moderator and control rods are necessary to operate a nuclear chain reaction safely for the purpose of energy production. Cite the function of each and explain why both are necessary.

53. Describe how the potential energy of uranium is converted into electrical energy in a nuclear power plant.

54. The mass of a hydrogen atom is 1.007825 amu; that of a tritium atom is 3.01605 amu; and that of an α particle is 4.00150 amu. How much energy in kilojoules per mole of produced is released by the following fusion reaction:

55. How can a radioactive nuclide be used to show that the equilibrium is a dynamic equilibrium?

56. Technetium-99m has a half-life of 6.01 hours. If a patient injected with technetium-99m is safe to leave the hospital once 75% of the dose has decayed, when is the patient allowed to leave?

57. Iodine that enters the body is stored in the thyroid gland from which it is released to control growth and metabolism. The thyroid can be imaged if iodine-131 is injected into the body. In larger doses, I-133 is also used as a means of treating cancer of the thyroid. I-131 has a half-life of 8.70 days and decays by β^- emission.

a. Write an equation for the decay.
b. How long will it take for 95.0% of a dose of I-131 to decay?

58. If a hospital were storing radioisotopes, what is the minimum containment needed to protect against:

a. cobalt-60 (a strong γ emitter used for irradiation)
b. molybdenum-99 (a beta emitter used to produce technetium-99 for imaging)

59. Based on what is known about Radon-222's primary decay method, why is inhalation so dangerous?

60. Given specimens uranium-232 ($t_{1/2}$ = 68.9 y) and uranium-233 ($t_{1/2}$ = 159,200 y) of equal mass, which one would have greater activity and why?

61. A scientist is studying a 2.234 g sample of thorium-229 ($t_{1/2}$ = 7340 y) in a laboratory.

a. What is its activity in Bq?
b. What is its activity in Ci?

62. Given specimens neon-24 ($t_{1/2}$ = 3.38 min) and bismuth-211 ($t_{1/2}$ = 2.14 min) of equal mass, which one would have greater activity and why?

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18.3: Nuclear Structure and Stability

Learning Objectives

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

- Describe nuclear structure in terms of protons, neutrons, and electrons
- Calculate mass defect and binding energy for nuclei
- Explain trends in the relative stability of nuclei

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of ${}^{1}_{1}\text{H}$.

Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term **nuclide** and identify it by the notation ${}^{Z}_{A}\text{X}$, where X is the symbol for the element, A is the mass number, and Z is the atomic number (for example, ${}^{14}_{6}\text{C}$). Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, ${}^{14}_{6}\text{C}$ is called "carbon-14."

Protons and neutrons, collectively called **nucleons**, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8×10^{14} grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of 22.6 g/cm3. If the earth's density were equal to the average nuclear density, the earth's radius would be only about 200 meters (earth's actual radius is approximately 6.4×10^{6} meters, 30,000 times larger). Example $18.3.1$ demonstrates just how great nuclear densities can be in the natural world.

Example 18.3.1: Density of a Neutron Star

Neutron stars form when the core of a very massive star undergoes gravitational collapse, causing the star's outer layers to explode in a supernova. Composed almost completely of neutrons, they are the densest-known stars in the universe, with densities comparable to the average density of an atomic nucleus. A neutron star in a faraway galaxy has a mass equal to 2.4 solar masses (1 solar mass = $M_{\odot}$ = mass of the sun = $1.99 \times 10^{30}\ kg$) and a diameter of 26 km.

a. What is the density of this neutron star?
b. How does this neutron star's density compare to the density of a uranium nucleus, which has a diameter of about 15 fm (1 fm = 10^{-15} m)?

Solution

We can treat both the neutron star and the U-235 nucleus as spheres. Then the density for both is given by:

$$d = \frac{m}{V} \quad \text{with} \quad V = \frac{4}{3}\pi r^3$$

a. The radius of the neutron star is so the density of the neutron star is:

$$d = \frac{m}{V} = \frac{m}{\frac{4}{3}\pi r^3} = \frac{2.4\left(1.99 \times 10^{30}\,\text{kg}\right)}{\frac{4}{3}\pi\left(1.3 \times 10^{4} m\right)^3} = 5.2 \times 10^{17}\,\text{kg/m}^3$$

b. The radius of the U-235 nucleus is so the density of the U-235 nucleus is:

$$d = \frac{m}{V} = \frac{m}{\frac{4}{3}\pi r^3} = \frac{235\,\text{amu}\left(\frac{1.66 \times 10^{-27}\,\text{kg}}{1\,\text{amu}}\right)}{\frac{4}{3}\pi\left(7.5 \times 10^{-15}\,\text{m}\right)^3} = 2.2 \times 10^{17}\,\text{kg/m}^3$$

These values are fairly similar (same order of magnitude), but the neutron star is more than twice as dense as the U-235 nucleus.

Exercise 18.3.1

Find the density of a neutron star with a mass of 1.97 solar masses and a diameter of 13 km, and compare it to the density of a hydrogen nucleus, which has a diameter of $1.75\ \text{fm}$ ($1\ \text{fm} = 1 \times 10^{-15}\ \text{m}$).

Answer

The density of the neutron star is $3.4 \times 10^{18}\ \text{kg/m}^3$. The density of a hydrogen nucleus is $\boxed{6.0 \times 10^{17}\ \text{kg/m}^3}$. The neutron star is 5.7 times denser than the hydrogen nucleus.

To hold positively charged protons together in the very small volume of a nucleus requires very strong attractive forces because the positively charged protons repel one another strongly at such short distances. The force of attraction that holds the nucleus together is the strong nuclear force. (The strong force is one of the four fundamental forces that are known to exist. The others are the electromagnetic force, the gravitational force, and the nuclear weak force.) This force acts between protons, between neutrons, and between protons and neutrons. It is very different from the electrostatic force that holds negatively charged electrons around a positively charged nucleus (the attraction between opposite charges). Over distances less than 10^{-15} meters and within the nucleus, the strong nuclear force is much stronger than electrostatic repulsions between protons; over larger distances and outside the nucleus, it is essentially nonexistent.

Link to Learning

Visit this website for more information about the four fundamental forces.

Nuclear Binding Energy

As a simple example of the energy associated with the strong nuclear force, consider the helium atom composed of two protons, two neutrons, and two electrons. The total mass of these six subatomic particles may be calculated as:

$$\underbrace{(2 \times 1.0073\ \text{amu})}_{\text{protons}} + \underbrace{(2 \times 1.0087\ \text{amu})}_{\text{neutrons}} + \underbrace{(2 \times 0.00055\ \text{amu})}_{\text{electrons}} = 4.0331\ \text{amu}$$

However, mass spectrometric measurements reveal that the mass of an atom is 4.0026 amu, less than the combined masses of its six constituent subatomic particles. This difference between the calculated and experimentally measured masses is known as the mass defect of the atom. In the case of helium, the **mass defect** indicates a "loss" in mass of 4.0331 amu – 4.0026 amu = 0.0305 amu. The loss in mass accompanying the formation of an atom from protons, neutrons, and electrons is due to the conversion of that mass into energy that is evolved as the atom forms. The **nuclear binding energy** is the energy produced when the atoms' nucleons are bound together; this is also the energy needed to break a nucleus into its constituent protons and neutrons. In comparison to chemical bond energies, nuclear binding energies are *vastly* greater, as we will learn in this section. Consequently, the energy changes associated with nuclear reactions are vastly greater than are those for chemical reactions.

The conversion between mass and energy is most identifiably represented by the **mass-energy equivalence equation** as stated by Albert Einstein:

$$E = mc^2 \tag{18.3.1}$$

where E is energy, m is mass of the matter being converted, and c is the speed of light in a vacuum. This equation can be used to find the amount of energy that results when matter is converted into energy. Using this mass-energy equivalence equation, the nuclear binding energy of a nucleus may be calculated from its mass defect, as demonstrated in Example 18.3.2 A variety of units are commonly used for nuclear binding energies, including electron volts (eV), with 1 eV equaling the amount of energy necessary to the move the charge of an electron across an electric potential difference of 1 volt, making 1 eV = 1.602 10^{-19} J.

Example 18.3.2: Calculation of Nuclear Binding Energy

Determine the binding energy for the nuclide in:

a. joules per mole of nuclei
b. joules per nucleus

c. MeV per nucleus

Solution

The mass defect for a ^4_2He nucleus is 0.0305 amu, as shown previously. Determine the binding energy in joules per nuclide using the mass-energy equivalence equation. To accommodate the requested energy units, the mass defect must be expressed in kilograms (recall that 1 J = 1 kg m^2/s^2).

a. First, express the mass defect in g/mol. This is easily done considering the *numerical equivalence* of atomic mass (amu) and molar mass (g/mol) that results from the definitions of the amu and mole units (refer to the previous discussion in the chapter on atoms, molecules, and ions if needed). The mass defect is therefore 0.0305 g/mol. To accommodate the units of the other terms in the mass-energy equation, the mass must be expressed in kg, since 1 J = 1 kg m^2/s^2. Converting grams into kilograms yields a mass defect of $3.05 \times 10^{-5}\ \text{kg/mol}$. Substituting this quantity into the mass-energy equivalence equation yields:

$$E = mc^2 = \frac{3.05 \times 10^{-5}\,kg}{mol} \times \left(\frac{2.998 \times 10^{8} m}{s}\right)^2 = 2.74 \times 10^{12}\ \text{kg m}^2\text{s}^{-2}\text{mol}^{-1}$$

$$= 2.74 \times 10^{12}\ \text{J mol}^{-1} = 2.74\ \text{TJ mol}^{-1}$$

Note that this tremendous amount of energy is associated with the conversion of a very small amount of matter (about 30 mg, roughly the mass of typical drop of water).

b. The binding energy for a single nucleus is computed from the molar binding energy using Avogadro's number:

$$E = 2.74 \times 10^{12}\ \text{J mol}^{-1} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{nuclei}}$$

$$= 4.55 \times 10^{-12}\ \text{J} = 4.55\ \text{pJ}$$

c. Recall that $1\ \text{eV} = 1.602 \times 10^{-19}\ \text{J}$. Using the binding energy computed in part (b):

$$E = 4.55 \times 10^{-12}\ \text{J} \times \frac{1\ \text{eV}}{1.602 \times 10^{-19}\ \text{J}} = 2.84 \times 10^{7}\ \text{eV} = 28.4\ \text{MeV}$$

? Exercise 18.3.1

What is the binding energy for the $^{19}_{9}\text{F}$ nuclide (atomic mass: 18.9984 amu) in MeV per nucleus?

Answer

148.4 MeV

Because the energy changes for breaking and forming bonds are so small compared to the energy changes for breaking or forming nuclei, the changes in mass during all ordinary chemical reactions are virtually undetectable. As described in the chapter on thermochemistry, the most energetic chemical reactions exhibit enthalpies on the order of *thousands* of kJ/mol, which is equivalent to mass differences in the nanogram range (10^{-9} g). On the other hand, nuclear binding energies are typically on the order of *billions* of kJ/mol, corresponding to mass differences in the milligram range (10^{-3} g).

Nuclear Stability

A nucleus is stable if it cannot be transformed into another configuration without adding energy from the outside. Of the thousands of nuclides that exist, about 250 are stable. A plot of the number of neutrons versus the number of protons for stable nuclei reveals that the stable isotopes fall into a narrow band. This region is known as the **band of stability** (also called the belt, zone, or valley of stability). The straight line in Figure 18.3.1 represents nuclei that have a 1:1 ratio of protons to neutrons (n:p ratio). Note that the lighter stable nuclei, in general, have equal numbers of protons and neutrons. For example, nitrogen-14 has seven protons and seven neutrons. Heavier stable nuclei, however, have increasingly more neutrons than protons. For example: iron-56 has 30 neutrons and 26 protons, an n:p ratio of 1.15, whereas the stable nuclide lead-207 has 125 neutrons and 82 protons, an n:p ratio equal to 1.52. This is because larger nuclei have more proton-proton repulsions, and require larger numbers of neutrons to provide compensating strong forces to overcome these electrostatic repulsions and hold the nucleus together.

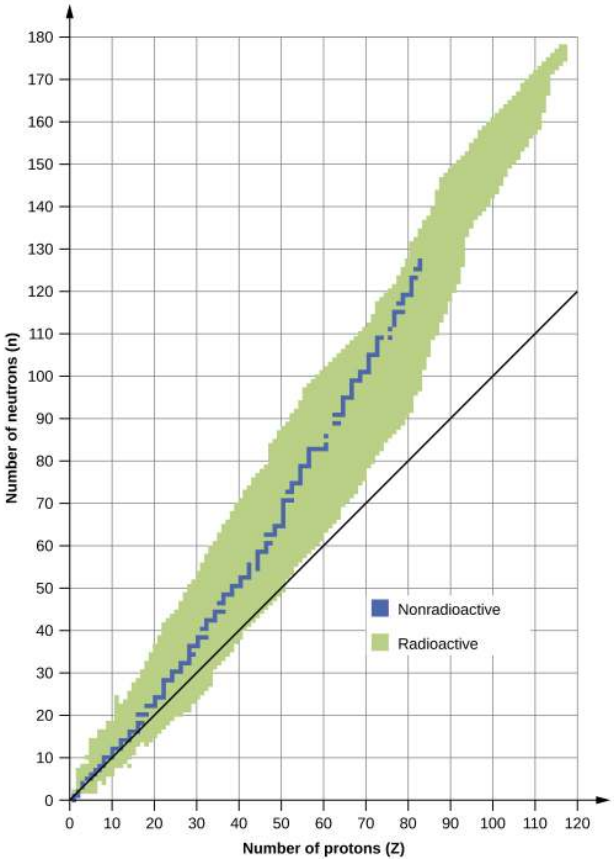


Figure 18.3.1: This plot shows the nuclides that are known to exist and those that are stable. The stable nuclides are indicated in blue, and the unstable nuclides are indicated in green. Note that all isotopes of elements with atomic numbers greater than 83 are unstable. The solid line is the line where n = Z.

The nuclei that are to the left or to the right of the band of stability are unstable and exhibit **radioactivity**. They change spontaneously (decay) into other nuclei that are either in, or closer to, the band of stability. These nuclear decay reactions convert one unstable isotope (or **radioisotope**) into another, more stable, isotope. We will discuss the nature and products of this radioactive decay in subsequent sections of this chapter.

Several observations may be made regarding the relationship between the stability of a nucleus and its structure. Nuclei with even numbers of protons, neutrons, or both are more likely to be stable (see Table 18.3.1). Nuclei with certain numbers of nucleons, known as **magic numbers**, are stable against nuclear decay. These numbers of protons or neutrons (2, 8, 20, 28, 50, 82, and 126) make complete shells in the nucleus. These are similar in concept to the stable electron shells observed for the noble gases. Nuclei that have magic numbers of both protons and neutrons, such as and are called “double magic” and are particularly stable. These trends in nuclear stability may be rationalized by considering a quantum mechanical model of nuclear energy states analogous to that used to describe electronic states earlier in this textbook. The details of this model are beyond the scope of this chapter.

Table 18.3.1: Stable Nuclear Isotopes

Number of Stable Isotopes	Proton Number	Neutron Number
157	even	even
53	even	odd
50	odd	even
5	odd	odd

The relative stability of a nucleus is correlated with its **binding energy per nucleon**, the total binding energy for the nucleus divided by the number or nucleons in the nucleus. For instance, we saw in Example 18.3.2 that the binding energy for a $^{4}_{2}\text{He}$

nucleus is 28.4 MeV. The *binding energy per nucleon* for a ^4_2He nucleus is therefore:

In Example 18.3.3, we learn how to calculate the binding energy per nucleon of a nuclide on the curve shown in Figure 18.3.2

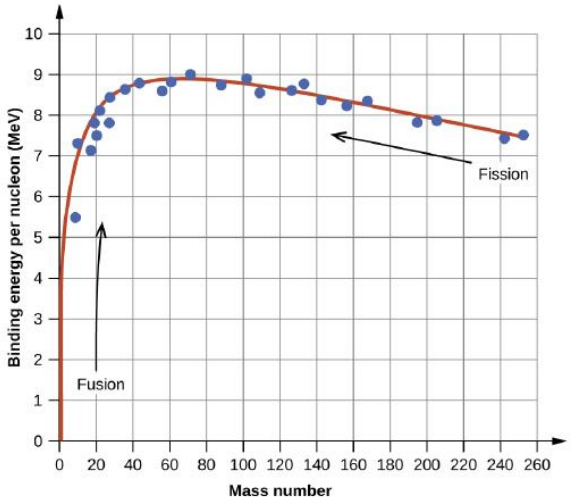


Figure 18.3.2: The binding energy per nucleon is largest for nuclides with mass number of approximately 56.

Example 18.3.3: Calculation of Binding Energy per Nucleon

The iron nuclide atom $^{56}_{26}\text{Fe}$ lies near the top of the binding energy curve (Figure 18.3.2) and is one of the most stable nuclides. What is the binding energy per nucleon (in MeV) for the nuclide $^{56}_{26}\text{Fe}$ (atomic mass of 55.9349 amu)?

Solution

As in Example 18.3.2, we first determine the mass defect of the nuclide, which is the difference between the mass of 26 protons, 30 neutrons, and 26 electrons, and the observed mass of an $^{56}_{26}\text{Fe}$ atom:

$$\begin{aligned}\text{Mass defect} &= [(26 \times 1.0073\ \text{amu}) + (30 \times 1.0087\ \text{amu}) + (26 \times 0.00055\ \text{amu})] - 55.9349 amu \\ &= 56.4651\ \text{amu} - 55.9349\ \text{amu} \\ &= 0.5302\ \text{amu}\end{aligned}$$

We next calculate the binding energy for one nucleus from the mass defect using the mass-energy equivalence equation:

$$\begin{aligned}E &= mc^2 = 0.5302\ \text{amu} \times \left(\frac{1.6605 \times 10^{-27}\ \text{kg}}{1\ \text{amu}}\right) \times \left(2.998 \times 10^8\ \text{m/s}\right)^2 \\ &= 7.913 \times 10^{-11}\ \text{kg} \cdot \text{m/s}^2 \\ &= 7.913 \times 10^{-11}\ \text{J}\end{aligned}$$

We then convert the binding energy in joules per nucleus into units of MeV per nuclide:

$$7.913 \times 10^{-11}\ \text{J} \times \frac{1\ \text{MeV}}{1.602 \times 10^{-13}\ \text{J}} = 493.9\ \text{MeV}$$

Finally, we determine the binding energy per nucleon by dividing the total nuclear binding energy by the number of nucleons in the atom:

Note that this is almost 25% larger than the binding energy per nucleon for ^4_2He.

$$\text{Binding energy per nucleon} = \frac{493.9\ \text{MeV}}{56} = 8.820\ \text{MeV/ nucleon}$$

(Note also that this is the same process as in Example 18.3.1, but with the additional step of dividing the total nuclear binding energy by the number of nucleons.)

Exercise 18.3.1

What is the binding energy per nucleon in $^{19}_{9}\mathrm{F}$ (atomic mass, 18.9984 amu)?

Answer

$7.810\ \mathrm{MeV/nucleon}$

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18.4: Nuclear Equations

Learning Objectives

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

- Identify common particles and energies involved in nuclear reactions
- Write and balance nuclear equations

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Types of Particles in Nuclear Reactions

Many entities can be involved in nuclear reactions. The most common are protons, neutrons, alpha particles, beta particles, positrons, and gamma rays, as shown in Figure 18.4.1. Protons ($_1^1\text{p}$, also represented by the symbol $_1^1\text{H}$) and neutrons ($_0^1\text{n}$) are the constituents of atomic nuclei, and have been described previously. **Alpha particles** ($_2^4\text{He}$, also represented by the symbol $_2^4\alpha$) are high-energy helium nuclei. **Beta particles** ($_{-1}^0\beta$, also represented by the symbol $_1^0\text{e}$) are high-energy electrons, and gamma rays are photons of very high-energy electromagnetic radiation. **Positrons** ($_{+1}^0\text{e}$, also represented by the symbol $_1^0\beta$) are positively charged electrons ("anti-electrons"). The subscripts and superscripts are necessary for balancing nuclear equations, but are usually optional in other circumstances. For example, an alpha particle is a helium nucleus (He) with a charge of +2 and a mass number of 4, so it is symbolized $_2^4\text{He}$. This works because, in general, the ion charge is not important in the balancing of nuclear equations.

Name	Symbol(s)	Representation	Description
Alpha particle	$_2^4\text{He}$ or $_2^4\alpha$		(High-energy) helium nuclei consisting of two protons and two neutrons
Beta particle	$_{-1}^0\text{e}$ or $_{-1}^0\beta$		(High-energy) electrons
Positron	$_{+1}^0\text{e}$ or $_{+1}^0\beta$		Particles with the same mass as an electron but with 1 unit of positive charge
Proton	$_1^1\text{H}$ or $_1^1\text{p}$		Nuclei of hydrogen atoms
Neutron	$_0^1\text{n}$		Particles with a mass approximately equal to that of a proton but with no charge
Gamma ray	γ		Very high-energy electromagnetic radiation

Figure 18.4.1: Although many species are encountered in nuclear reactions, this table summarizes the names, symbols, representations, and descriptions of the most common of these.

Note that positrons are exactly like electrons, except they have the opposite charge. They are the most common example of **antimatter**, particles with the same mass but the opposite state of another property (for example, charge) than ordinary matter. When antimatter encounters ordinary matter, both are annihilated and their mass is converted into energy in the form of **gamma rays** (γ)—and other much smaller subnuclear particles, which are beyond the scope of this chapter—according to the mass-energy equivalence equation $E = mc^2$, seen in the preceding section. For example, when a positron and an electron collide, both are annihilated and two gamma ray photons are created:

$$_{-1}^0\text{e} + _{+1}^0\text{e} \longrightarrow \gamma + \gamma$$

As seen in the chapter discussing light and electromagnetic radiation, gamma rays compose short wavelength, high-energy electromagnetic radiation and are (much) more energetic than better-known X-rays that can behave as particles in the wave-particle duality sense. Gamma rays are a type of high energy electromagnetic radiation produced when a nucleus undergoes a transition from a higher to a lower energy state, similar to how a photon is produced by an electronic transition from a higher to a lower

energy level. Due to the much larger energy differences between nuclear energy shells, gamma rays emanating from a nucleus have energies that are typically millions of times larger than electromagnetic radiation emanating from electronic transitions.

Balancing Nuclear Reactions

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of nucleons (subatomic particles within the atoms' nuclei) rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that ${}^{17}_{8}\mathrm{O}$ is a product of the nuclear reaction of ${}^{14}_{7}\mathrm{N}$ and ${}^{4}_{2}\mathrm{He}$ if we knew that a proton, ${}^{1}_{1}\mathrm{H}$, were one of the two products. Example 18.4.1 shows how we can identify a nuclide by balancing the nuclear reaction.

Example 18.4.1: Balancing Equations for Nuclear Reactions

The reaction of an α particle with magnesium-25 (${}^{25}_{12}\mathrm{Mg}$) produces a proton and a nuclide of another element. Identify the new nuclide produced.

Solution

The nuclear reaction can be written as:

$$ {}^{25}_{12}\mathrm{Mg} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{1}_{1}\mathrm{H} + {}^{A}_{Z}\mathrm{X} $$

where A is the mass number and Z is the atomic number of the new nuclide, X. Because the sum of the mass numbers of the reactants must equal the sum of the mass numbers of the products:

$$ 25 + 4 = A + 1 $$

or $A = 28$.

Similarly, the charges must balance, so:

$$ 12 + 2 = Z + 1 $$

and $Z = 13$.

Check the periodic table: The element with nuclear charge = +13 is aluminum. Thus, the product is ${}^{28}_{13}\mathrm{Al}$

Exercise 18.4.1

The nuclide ${}^{125}_{53}\mathrm{I}$ combines with an electron and produces a new nucleus and no other massive particles. What is the equation for this reaction?

Answer

$$ {}^{125}_{53}\mathrm{I} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{125}_{52}\mathrm{Te} $$

Following are the equations of several nuclear reactions that have important roles in the history of nuclear chemistry:

- The first naturally occurring unstable element that was isolated, polonium, was discovered by the Polish scientist Marie Curie and her husband Pierre in 1898. It decays, emitting α particles:

$$ {}^{212}_{84}\mathrm{Po} \longrightarrow {}^{208}_{82}\mathrm{Pb} + {}^{4}_{2}\mathrm{He} $$

- The first nuclide to be prepared by artificial means was an isotope of oxygen, ${}^{17}\mathrm{O}$. It was made by Ernest Rutherford in 1919 by bombarding nitrogen atoms with α particles:

$$^{14}_{7}\mathrm{N} + ^{4}_{2}\mathrm{He} \longrightarrow ^{17}_{8}\mathrm{O} + ^{1}_{1}\mathrm{H}$$

- James Chadwick discovered the neutron in 1932, as a previously unknown neutral particle produced along with ^{12}C by the nuclear reaction between ^{9}Be and ^{4}He:

$$^{9}_{4}\mathrm{Be} + ^{4}_{2}\mathrm{He} \longrightarrow ^{12}_{6}\mathrm{C} + ^{1}_{0}\mathrm{n}$$

- The first element to be prepared that does not occur naturally on the earth, technetium, was created by bombardment of molybdenum by deuterons (heavy hydrogen, $^{2}_{1}H$), by Emilio Segre and Carlo Perrier in 1937:

$$^{2}_{1}\mathrm{H} + ^{97}_{42}\mathrm{Mo} \longrightarrow 2\,^{1}_{0}\mathrm{n} + ^{97}_{43}\mathrm{Tc}$$

- The first controlled nuclear chain reaction was carried out in a reactor at the University of Chicago in 1942. One of the many reactions involved was:

$$^{235}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n} \longrightarrow ^{87}_{35}\mathrm{Br} + ^{146}_{57}\mathrm{La} + 3\,^{1}_{0}\mathrm{n}$$

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18.5: Radioactive Decay

Learning Objectives

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

- Recognize common modes of radioactive decay
- Identify common particles and energies involved in nuclear decay reactions
- Write and balance nuclear decay equations
- Calculate kinetic parameters for decay processes, including half-life
- Describe common radiometric dating techniques

Following the somewhat serendipitous discovery of radioactivity by Becquerel, many prominent scientists began to investigate this new, intriguing phenomenon. Among them were Marie Curie (the first woman to win a Nobel Prize, and the only person to win two Nobel Prizes in different sciences—chemistry and physics), who was the first to coin the term "radioactivity," and Ernest Rutherford (of gold foil experiment fame), who investigated and named three of the most common types of radiation. During the beginning of the twentieth century, many radioactive substances were discovered, the properties of radiation were investigated and quantified, and a solid understanding of radiation and nuclear decay was developed.

The spontaneous change of an unstable nuclide into another is **radioactive decay**. The unstable nuclide is called the **parent nuclide**; the nuclide that results from the decay is known as the **daughter nuclide**. The daughter nuclide may be stable, or it may decay itself. The radiation produced during radioactive decay is such that the daughter nuclide lies closer to the band of stability than the parent nuclide, so the location of a nuclide relative to the band of stability can serve as a guide to the kind of decay it will undergo (Figure 18.5.1).

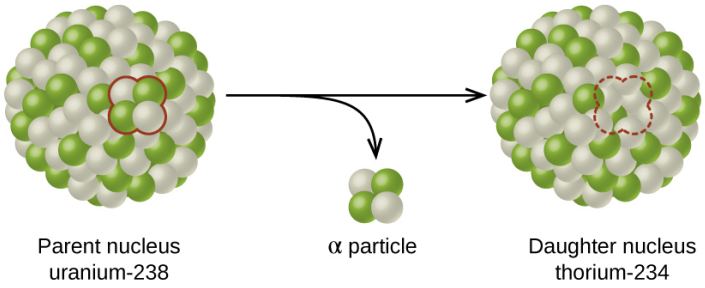


Figure 18.5.1: A nucleus of uranium-238 (the parent nuclide) undergoes α decay to form thorium-234 (the daughter nuclide). The alpha particle removes two protons (green) and two neutrons (gray) from the uranium-238 nucleus.

Link to Learning

Although the radioactive decay of a nucleus is too small to see with the naked eye, we can indirectly view radioactive decay in an environment called a cloud chamber. Click here to learn about cloud chambers and to view an interesting Cloud Chamber Demonstration from the Jefferson Lab.

Types of Radioactive Decay

Ernest Rutherford's experiments involving the interaction of radiation with a magnetic or electric field (Figure 18.5.2) helped him determine that one type of radiation consisted of positively charged and relatively massive α particles; a second type was made up of negatively charged and much less massive β particles; and a third was uncharged electromagnetic waves, γ rays. We now know that α particles are high-energy helium nuclei, β particles are high-energy electrons, and γ radiation compose high-energy electromagnetic radiation. We classify different types of radioactive decay by the radiation produced.

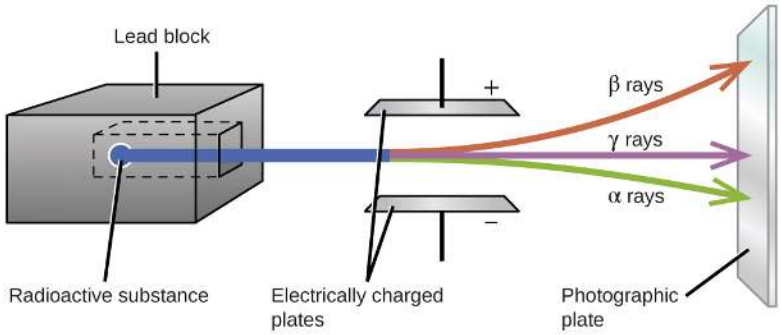


Figure 18.5.2: Alpha particles, which are attracted to the negative plate and deflected by a relatively small amount, must be positively charged and relatively massive. Beta particles, which are attracted to the positive plate and deflected a relatively large amount, must be negatively charged and relatively light. Gamma rays, which are unaffected by the electric field, must be uncharged.

Alpha (α) decay is the emission of an α particle from the nucleus. For example, polonium-210 undergoes α decay:

$$^{210}_{84}\mathrm{Po} \longrightarrow ^{4}_{2}\mathrm{He} + ^{206}_{82}\mathrm{Pb}$$

or

$$^{210}_{84}\mathrm{Po} \longrightarrow ^{4}_{2}\alpha + ^{206}_{82}\mathrm{Pb}$$

Alpha decay occurs primarily in heavy nuclei ($A > 200$, $Z > 83$). Because the loss of an α particle gives a daughter nuclide with a mass number four units smaller and an atomic number two units smaller than those of the parent nuclide, the daughter nuclide has a larger n:p ratio than the parent nuclide. If the parent nuclide undergoing α decay lies below the band of stability (refer to Figure 21.2), the daughter nuclide will lie closer to the band.

Beta (β) decay is the emission of an electron (i.e., a β particle) from a nucleus. Iodine-131 is an example of a nuclide that undergoes β decay:

$$^{131}_{53}\mathrm{I} \longrightarrow ^{0}_{-1}\mathrm{e} + ^{131}_{54}\mathrm{Xe}$$

or

$$^{131}_{53}\mathrm{I} \longrightarrow ^{0}_{-1}\beta + ^{131}_{54}\mathrm{Xe}$$

Beta decay, which can be thought of as the conversion of a neutron into a proton and a β particle, is observed in nuclides with a large n:p ratio. The beta particle (electron) emitted is from the atomic nucleus and is not one of the electrons surrounding the nucleus. Such nuclei lie above the band of stability. Emission of an electron does not change the mass number of the nuclide but does increase the number of its protons and decrease the number of its neutrons. Consequently, the n:p ratio is decreased, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Gamma emission (γ emission) is observed when a nuclide is formed in an excited state and then decays to its ground state with the emission of a γ ray, a quantum of high-energy electromagnetic radiation. The presence of a nucleus in an excited state is often indicated by an asterisk (*). Cobalt-60 emits γ radiation and is used in many applications including cancer treatment:

$$^{60}_{27}\mathrm{Co}^{\cdot} \longrightarrow ^{0}_{0}\gamma + ^{60}_{27}\mathrm{Co}$$

There is no change in mass number or atomic number during the emission of a γ ray unless the γ emission accompanies one of the other modes of decay.

Positron emission (β^+ decay) is the emission of a positron from the nucleus. Oxygen-15 is an example of a nuclide that undergoes positron emission:

$$^{15}_{8}\mathrm{O} \longrightarrow ^{0}_{+1}\mathrm{e} + ^{15}_{7}\mathrm{N}$$

or

$$^{15}_{8}\mathrm{O} \longrightarrow ^{0}_{+1}\beta + ^{15}_{7}\mathrm{N}$$

Positron emission is observed for nuclides in which the n:p ratio is low. These nuclides lie below the band of stability. Positron decay is the conversion of a proton into a neutron with the emission of a positron. The n:p ratio increases, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Electron capture occurs when one of the inner electrons in an atom is captured by the atom's nucleus. For example, potassium-40 undergoes electron capture:

$$^{40}_{19}\mathrm{K} + ^{0}_{-1}\mathrm{e} \longrightarrow ^{40}_{18}\mathrm{Ar}$$

Electron capture occurs when an inner shell electron combines with a proton and is converted into a neutron. The loss of an inner shell electron leaves a vacancy that will be filled by one of the outer electrons. As the outer electron drops into the vacancy, it will emit energy. In most cases, the energy emitted will be in the form of an X-ray. Like positron emission, electron capture occurs for "proton-rich" nuclei that lie below the band of stability. Electron capture has the same effect on the nucleus as does positron emission: The atomic number is decreased by one and the mass number does not change. This increases the n:p ratio, and the daughter nuclide lies closer to the band of stability than did the parent nuclide. Whether electron capture or positron emission occurs is difficult to predict. The choice is primarily due to kinetic factors, with the one requiring the smaller activation energy being the one more likely to occur.

Figure 18.5.3 summarizes these types of decay, along with their equations and changes in atomic and mass numbers.

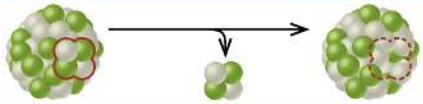
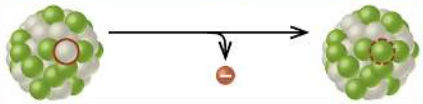
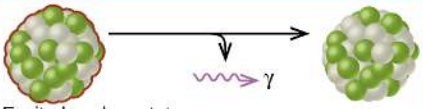
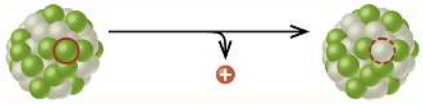
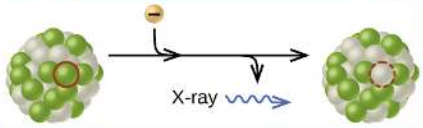
Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	$^{A}_{Z}\mathrm{X} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{A-4}_{Z-2}\mathrm{Y}$		A: decrease by 4 Z: decrease by 2
Beta decay	$^{A}_{Z}\mathrm{X} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{A}_{Z+1}\mathrm{Y}$		A: unchanged Z: increase by 1
Gamma decay	$^{A}_{Z}\mathrm{X} \rightarrow {}^{0}_{0}\gamma + {}^{A}_{Z}\mathrm{Y}$		A: unchanged Z: unchanged
Positron emission	$^{A}_{Z}\mathrm{X} \rightarrow {}^{0}_{+1}\mathrm{e} + {}^{A}_{Y-1}\mathrm{Y}$		A: unchanged Z: decrease by 1
Electron capture	$^{A}_{Z}\mathrm{X} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{A}_{Y-1}\mathrm{Y}$		A: unchanged Z: decrease by 1

Figure 18.5.3: This table summarizes the type, nuclear equation, representation, and any changes in the mass or atomic numbers for various types of decay.

Chemistry in Everyday Life: PET Scan

Positron emission tomography (PET) scans use radiation to diagnose and track health conditions and monitor medical treatments by revealing how parts of a patient's body function (Figure 18.5.4). To perform a PET scan, a positron-emitting radioisotope is produced in a cyclotron and then attached to a substance that is used by the part of the body being investigated. This "tagged" compound, or radiotracer, is then put into the patient (injected via IV or breathed in as a gas), and how it is used by the tissue reveals how that organ or other area of the body functions.

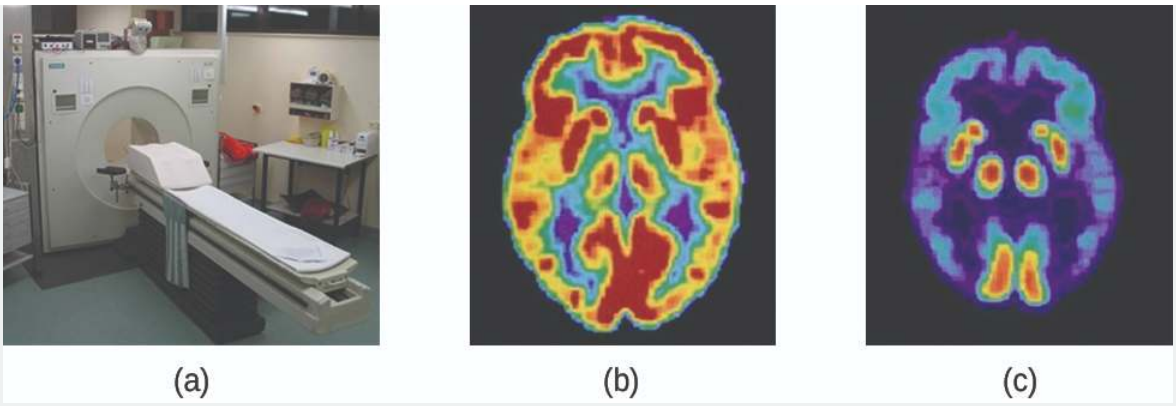


Figure 18.5.4: A PET scanner (a) uses radiation to provide an image of how part of a patient's body functions. The scans it produces can be used to image a healthy brain (b) or can be used for diagnosing medical conditions such as Alzheimer's disease (c). (credit a: modification of work by Jens Maus)

For example, F-18 is produced by proton bombardment of \(\ce{^{18}O}\)

$$^{18}_{8}\mathrm{O} + ^{1}_{1}\mathrm{p} \longrightarrow ^{18}_{9}\mathrm{F} + ^{1}_{0}\mathrm{n}$$

and incorporated into a glucose analog called fludeoxyglucose (FDG). How FDG is used by the body provides critical diagnostic information; for example, since cancers use glucose differently than normal tissues, FDG can reveal cancers. The $^{18}\mathrm{F}$ emits positrons that interact with nearby electrons, producing a burst of gamma radiation. This energy is detected by the scanner and converted into a detailed, three-dimensional, color image that shows how that part of the patient's body functions. Different levels of gamma radiation produce different amounts of brightness and colors in the image, which can then be interpreted by a radiologist to reveal what is going on. PET scans can detect heart damage and heart disease, help diagnose Alzheimer's disease, indicate the part of a brain that is affected by epilepsy, reveal cancer, show what stage it is, and how much it has spread, and whether treatments are effective. Unlike magnetic resonance imaging and X-rays, which only show how something looks, the big advantage of PET scans is that they show how something functions. PET scans are now usually performed in conjunction with a computed tomography scan.

Radioactive Decay Series

The naturally occurring radioactive isotopes of the heaviest elements fall into chains of successive disintegrations, or decays, and all the species in one chain constitute a radioactive family, or **radioactive decay series**. Three of these series include most of the naturally radioactive elements of the periodic table. They are the uranium series, the actinide series, and the thorium series. The neptunium series is a fourth series, which is no longer significant on the earth because of the short half-lives of the species involved. Each series is characterized by a parent (first member) that has a long half-life and a series of daughter nuclides that ultimately lead to a stable end-product—that is, a nuclide on the band of stability (Figure 18.5.5). In all three series, the end-product is a stable isotope of lead. The neptunium series, previously thought to terminate with bismuth-209, terminates with thallium-205.

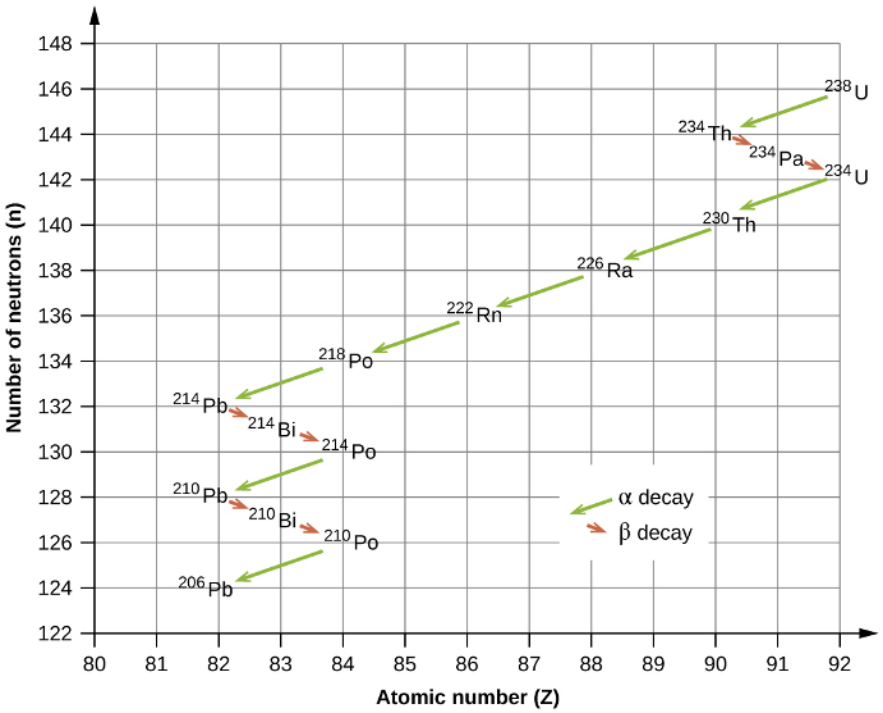


Figure 18.5.5: Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight α decays and six β decays.

Radioactive Half-Lives

Radioactive decay follows first-order kinetics. Since first-order reactions have already been covered in detail in the kinetics chapter, we will now apply those concepts to nuclear decay reactions. Each radioactive nuclide has a characteristic, constant **half-life** ($t_{1/2}$), the time required for half of the atoms in a sample to decay. An isotope's half-life allows us to determine how long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, coba source, since half of the nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

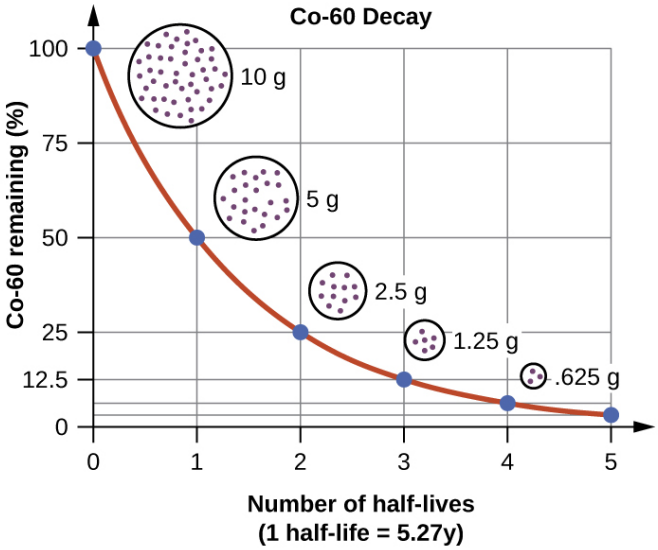


Figure 18.5.6: For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

Since nuclear decay follows first-order kinetics, we can adapt the mathematical relationships used for first-order chemical reactions. We generally substitute the number of nuclei, N, for the concentration. If the rate is stated in nuclear decays per second, we refer to it as the **activity** of the radioactive sample. The rate for radioactive decay is:

$$\text{decay rate} = \lambda N$$

with λ = the decay constant for the particular radioisotope.

The decay constant, λ, which is the same as a rate constant discussed in the kinetics chapter. It is possible to express the decay constant in terms of the half-life, $t_{1/2}$:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}}$$

or

$$t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

The first-order equations relating amount, N, and time are:

$$N_t = N_0 e^{-\lambda t} \tag{18.5.1}$$

or

$$t = -\frac{1}{\lambda} \ln\left(\frac{N_t}{N_0}\right)$$

Example 18.5.1: Rates of Radioactive Decay

$^{60}_{27}\text{Co}$ decays with a half-life of 5.27 years to produce $^{60}_{28}\text{Co}$

a. What is the decay constant for the radioactive disintegration of cobalt-60?
b. Calculate the fraction of a sample of the $^{60}_{27}\text{Co}$ isotope that will remain after 15 years.
c. How long does it take for a sample of $^{60}_{27}\text{Co}$ to disintegrate to the extent that only 2.0% of the original amount remains?

Solution

(a) The value of the rate constant is given by:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5.27y} = 0.132y^{-1}$$

(b) The fraction of $^{60}_{27}\text{Co}$ that is left after time t is given by $\frac{N_t}{N_0}$. Rearranging the first-order relationship in Equation 18.5.1 ($N_t = N_0 e^{-\lambda t}$ to solve for this ratio yields:

$$\frac{N_t}{N_0} = e^{-\lambda t} = e^{-(0.132/\text{y})(15\ \text{y})} = 0.138$$

The fraction of $^{60}_{27}\text{Co}$ that will remain after 15.0 years is 0.138. Or put another way, 13.8% of the original $^{60}_{27}\text{Co}$ present will remain after 15 years.

(c) 2.00% of the original amount of $^{60}_{27}\text{Co}$ is equal to 0.0200 N_0. Substituting this into the equation for time for first-order kinetics, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) = -\frac{1}{0.132\ \text{y}^{-1}}\ln\left(\frac{0.0200 \times N_0}{N_0}\right) = 29.6y$$

? Exercise 18.5.1

Radon-222, $^{222}_{86}\text{Rn}$ has a half-life of 3.823 days. How long will it take a sample of radon-222 with a mass of 0.750 g to decay into other elements, leaving only 0.100 g of radon-222?

Answer

11.1 days

Because each nuclide has a specific number of nucleons, a particular balance of repulsion and attraction, and its own degree of stability, the half-lives of radioactive nuclides vary widely. For example: the half-life of $^{209}_{83}\text{Bi}$ is 1.9×10^{19} years; $^{239}_{94}\text{Ra}$ is 24,000 years; $^{222}_{86}\text{Rn}$ is 3.82 days; and element-111 (Rg for roentgenium) is 1.5×10^{-3} seconds. The half-lives of a number of radioactive isotopes important to medicine are shown in Table 18.5.1, and others are listed in Appendix M.

Table 18.5.1: Half-lives of Radioactive Isotopes Important to Medicine

Type[1]	Decay Mode	Half-Life	Uses
F-18	β^+ decay	110. minutes	PET scans
Co-60	β decay, γ decay	5.27 years	cancer treatment
Tc-99m	γ decay	8.01 hours	scans of brain, lung, heart, bone
I-131	β decay	8.02 days	thyroid scans and treatment
Tl-201	electron capture	73 hours	heart and arteries scans; cardiac stress tests

Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of “dating” the origin of objects such as archaeological artifacts, formerly living organisms, or geological formations. This process is **radiometric dating** and has been responsible for many breakthrough scientific discoveries about the geological history of the earth, the evolution of life, and the history of human civilization. We will explore some of the most common types of radioactive dating and how the particular isotopes work for each type.

Radioactive Dating Using Carbon-14

The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called **radiocarbon dating** or carbon-14 dating, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes: ${}^{12}_{6}\mathrm{C}$ which constitutes about 99% of the carbon on earth; ${}^{13}_{6}\mathrm{C}$, about 1% of the total; and trace amounts of ${}^{14}_{6}\mathrm{C}$. Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:

$$ {}^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H} $$

All isotopes of carbon react with oxygen to produce CO_2 molecules. The ratio of ${}^{14}_{6}\mathrm{CO}_2$ to ${}^{12}_{6}\mathrm{CO}_2$ depends on the ratio of ${}^{14}_{6}\mathrm{CO}$ to ${}^{12}_{6}\mathrm{CO}$ in the atmosphere. The natural abundance of ${}^{14}_{6}\mathrm{CO}$ in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen is gas samples found trapped in ice. The incorporation of ${}^{14}_{6}\mathrm{CO}_2$ and ${}^{14}_{6}\mathrm{CO}_2$ into plants is a regular part of the photosynthesis process, which means that the ${}^{14}_{6}\mathrm{C} : {}^{12}_{6}\mathrm{C}$ ratio found in a living plant is the **same** as the ${}^{14}_{6}\mathrm{C} : {}^{12}_{6}\mathrm{C}$ ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because ${}^{12}_{6}\mathrm{C}$ is a stable isotope and does not undergo radioactive decay, its concentration in the plant does not change. However, carbon-14 decays by β emission with a half-life of 5730 years:

$$ {}^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e} $$

Thus, the ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant). Figure 18.5.7: visually depicts this process.

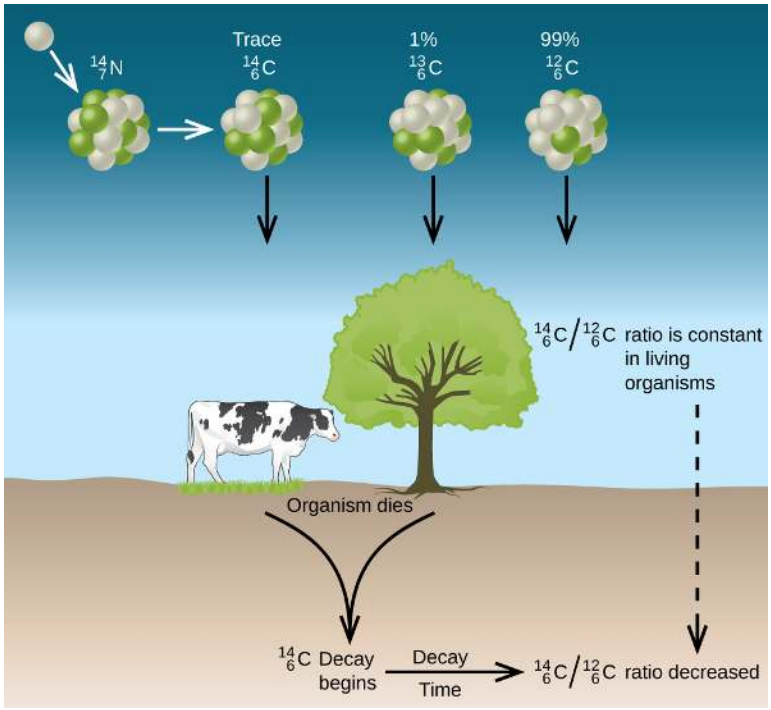


Figure 18.5.7: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died).

For example, with the half-life of being 5730 years, if the ratio in a wooden object found in an archaeological dig is half what it is in a living tree, this indicates that the wooden object is 5730 years old. Highly accurate determinations of ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

Link to Learning

Visit this website to perform simulations of radiometric dating.

Example 18.5.2: Radiocarbon Dating

A tiny piece of paper (produced from formerly living plant matter) taken from the Dead Sea Scrolls has an activity of 10.8 disintegrations per minute per gram of carbon. If the initial C-14 activity was 13.6 disintegrations/min/g of C, estimate the age of the Dead Sea Scrolls.

Solution

The rate of decay (number of disintegrations/minute/gram of carbon) is proportional to the amount of radioactive C-14 left in the paper, so we can substitute the rates for the amounts, N, in the relationship:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) \longrightarrow t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_t}{\text{Rate}_0}\right)$$

where the subscript 0 represents the time when the plants were cut to make the paper, and the subscript t represents the current time.

The decay constant can be determined from the half-life of C-14, 5730 years:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5730\ \text{y}} = 1.21 \times 10^{-4}\ \text{y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_t}{\text{Rate}_0}\right) = -\frac{1}{1.21 \times 10^{-4}\ \text{y}^{-1}}\ln\left(\frac{10.8\ \text{dis/min/g C}}{13.6\ \text{dis/min/g C}}\right) = 1910\ \text{y}$$

Therefore, the Dead Sea Scrolls are approximately 1900 years old (Figure 18.5.8).



Figure 18.5.8: Carbon-14 dating has shown that these pages from the Dead Sea Scrolls were written or copied on paper made from plants that died between 100 BC and AD 50.

Exercise 18.5.1

More accurate dates of the reigns of ancient Egyptian pharaohs have been determined recently using plants that were preserved in their tombs. Samples of seeds and plant matter from King Tutankhamun's tomb have a C-14 decay rate of 9.07 disintegrations/min/g of C. How long ago did King Tut's reign come to an end?

Answer

about 3350 years ago, or approximately 1340 BC

There have been some significant, well-documented changes to the ${}^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ ratio. The accuracy of a straightforward application of this technique depends on the ${}^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ ratio in a living plant being the same now as it was in an earlier era, but this is not always valid. Due to the increasing accumulation of CO_2 molecules (largely ${}^{12}_{6}\text{C}$) in the atmosphere caused by combustion of fossil fuels (in which essentially all of the ${}^{14}_{6}\text{C}$ has decayed), the ratio of ${}^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ in the atmosphere may be changing. This manmade increase in ${}^{12}_{6}\text{C}$ in the atmosphere causes the ${}^{14}_{6}\text{C} : {}^{12}_{6}\text{C}$ ratio to decrease, and this in turn affects the ratio in currently living organisms on the earth. Fortunately, however, we can use other data, such as tree dating via examination of annual growth rings, to calculate correction factors. With these correction factors, accurate dates can be determined. In general, radioactive dating only works for about 10 half-lives; therefore, the limit for carbon-14 dating is about 57,000 years.

Radioactive Dating Using Nuclides Other than Carbon-14

Radioactive dating can also use other radioactive nuclides with longer half-lives to date older events. For example, uranium-238 (which decays in a series of steps into lead-206) can be used for establishing the age of rocks (and the approximate age of the oldest rocks on earth). Since U-238 has a half-life of 4.5 billion years, it takes that amount of time for half of the original U-238 to decay into Pb-206. In a sample of rock that does not contain appreciable amounts of Pb-208, the most abundant isotope of lead, we can assume that lead was not present when the rock was formed. Therefore, by measuring and analyzing the ratio of U-238:Pb-206, we can determine the age of the rock. This assumes that all of the lead-206 present came from the decay of uranium-238. If there is additional lead-206 present, which is indicated by the presence of other lead isotopes in the sample, it is necessary to make an adjustment. Potassium-argon dating uses a similar method. K-40 decays by positron emission and electron capture to form Ar-40 with a half-life of 1.25 billion years. If a rock sample is crushed and the amount of Ar-40 gas that escapes is measured, determination of the Ar-40:K-40 ratio yields the age of the rock. Other methods, such as rubidium-strontium dating (Rb-87 decays into Sr-87 with a half-life of 48.8 billion years), operate on the same principle. To estimate the lower limit for the earth's age, scientists determine the age of various rocks and minerals, making the assumption that the earth is older than the oldest rocks and minerals in its crust. As of 2014, the oldest known rocks on earth are the Jack Hills zircons from Australia, found by uranium-lead dating to be almost 4.4 billion years old.

Example 18.5.3: Radioactive Dating of Rocks

An igneous rock contains 9.58×10^{-5} g of U-238 and 2.51×10^{-5} g of Pb-206, and much, much smaller amounts of Pb-208. Determine the approximate time at which the rock formed.

Solution

The sample of rock contains very little Pb-208, the most common isotope of lead, so we can safely assume that all the Pb-206 in the rock was produced by the radioactive decay of U-238. When the rock formed, it contained all of the U-238 currently in it, plus some U-238 that has since undergone radioactive decay.

The amount of U-238 currently in the rock is:

$$9.58 \times 10^{-5} \ \cancel{\text{g U}} \times \left(\frac{1 \text{ mol U}}{238 \ \cancel{\text{g U}}} \right) = 4.03 \times 10^{-7} \text{ mol U}$$

Because when one mole of U-238 decays, it produces one mole of Pb-206, the amount of U-238 that has undergone radioactive decay since the rock was formed is:

$$2.51 \times 10^{-5} \ \cancel{\text{g Pb}} \times \left(\frac{1 \ \cancel{\text{mol Pb}}}{206 \ \cancel{\text{g Pb}}} \right) \times \left(\frac{1 \text{ mol U}}{1 \ \cancel{\text{mol Pb}}} \right) = 1.22 \times 10^{-7} \text{ mol U}$$

The total amount of U-238 originally present in the rock is therefore:

$$4.03 \times 10^{-7} \text{ mol U} + 1.22 \times 10^{-7} \text{ mol U} = 5.25 \times 10^{-7} \text{ mol U}$$

The amount of time that has passed since the formation of the rock is given by:

$$t = -\frac{1}{\lambda} \ln \left(\frac{N_t}{N_0} \right)$$

with N_0 representing the original amount of U-238 and N_t representing the present amount of U-238.

U-238 decays into Pb-206 with a half-life of 4.5×10^9 y, so the decay constant λ is:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9 \text{ y}} = 1.54 \times 10^{-10} \text{ y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{1.54 \times 10^{-10} \text{ y}^{-1}} \ln \left(\frac{4.03 \times 10^{-7} \ \cancel{\text{mol U}}}{5.25 \times 10^{-7} \ \cancel{\text{mol U}}} \right) = 1.7 \times 10^9 \text{ y}$$

Therefore, the rock is approximately 1.7 billion years old.

Exercise 18.5.1

A sample of rock contains 6.14×10^{-4} g of Rb-87 and $3.51 \times 10^{-5} g$ of Sr-87. Calculate the age of the rock. (The half-life of the β decay of Rb-87 is 4.7×10^{10} y.)

Answer

3.7 10^9 y

Footnotes

- 1The “m” in Tc-99m stands for “metastable,” indicating that this is an unstable, high-energy state of Tc-99. Metastable isotopes emit γ radiation to rid themselves of excess energy and become (more) stable.

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18.6: Transmutation and Nuclear Energy

Learning Objectives

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

- Describe the synthesis of transuranium nuclides
- Explain nuclear fission and fusion processes
- Relate the concepts of critical mass and nuclear chain reactions
- Summarize basic requirements for nuclear fission and fusion reactors

After the discovery of radioactivity, the field of nuclear chemistry was created and developed rapidly during the early twentieth century. A slew of new discoveries in the 1930s and 1940s, along with World War II, combined to usher in the Nuclear Age in the mid-twentieth century. Scientists learned how to create new substances, and certain isotopes of certain elements were found to possess the capacity to produce unprecedented amounts of energy, with the potential to cause tremendous damage during war, as well as produce enormous amounts of power for society's needs during peace.

Synthesis of Nuclides

Nuclear transmutation is the conversion of one nuclide into another. It can occur by the radioactive decay of a nucleus, or the reaction of a nucleus with another particle. The first manmade nucleus was produced in Ernest Rutherford's laboratory in 1919 by a transmutation reaction, the bombardment of one type of nuclei with other nuclei or with neutrons. Rutherford bombarded nitrogen atoms with high-speed α particles from a natural radioactive isotope of radium and observed protons resulting from the reaction:

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$$

The $^{17}_{8}\mathrm{O}$ and $^{14}_{7}\mathrm{N}$ nuclei that are produced are stable, so no further (nuclear) changes occur.

To reach the kinetic energies necessary to produce transmutation reactions, devices called **particle accelerators** are used. These devices use magnetic and electric fields to increase the speeds of nuclear particles. In all accelerators, the particles move in a vacuum to avoid collisions with gas molecules.

When neutrons are required for transmutation reactions, they are usually obtained from radioactive decay reactions or from various nuclear reactions occurring in nuclear reactors. The Chemistry in Everyday Life feature that follows discusses a famous particle accelerator that made worldwide news.

Chemistry in Everyday Life: CERN Particle Accelerator

Located near Geneva, the CERN ("Conseil Européen pour la Recherche Nucléaire," or European Council for Nuclear Research) Laboratory is the world's premier center for the investigations of the fundamental particles that make up matter. It contains the 27-kilometer (17 mile) long, circular Large Hadron Collider (LHC), the largest particle accelerator in the world (Figure 18.6.1). In the LHC, particles are boosted to high energies and are then made to collide with each other or with stationary targets at nearly the speed of light. Superconducting electromagnets are used to produce a strong magnetic field that guides the particles around the ring. Specialized, purpose-built detectors observe and record the results of these collisions, which are then analyzed by CERN scientists using powerful computers.



Figure 18.6.1: A small section of the LHC is shown with workers traveling along it. (credit: Christophe Delaere)

In 2012, CERN announced that experiments at the LHC showed the first observations of the Higgs boson, an elementary particle that helps explain the origin of mass in fundamental particles. This long-anticipated discovery made worldwide news and resulted in the awarding of the 2013 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

Link to Learning

Famous physicist Brian Cox talks about his work on the Large Hadron Collider at CERN, providing an entertaining and engaging tour of this massive project and the physics behind it.

View a short video from CERN, describing the basics of how its particle accelerators work.

Prior to 1940, the heaviest-known element was uranium, whose atomic number is 92. Now, many artificial elements have been synthesized and isolated, including several on such a large scale that they have had a profound effect on society. One of these—element 93, neptunium (Np)—was first made in 1940 by McMillan and Abelson by bombarding uranium-238 with neutrons. The reaction creates unstable uranium-239, with a half-life of 23.5 minutes, which then decays into neptunium-239. Neptunium-239 is also radioactive, with a half-life of 2.36 days, and it decays into plutonium-239. The nuclear reactions are:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U}$$

$$^{239}_{92}\mathrm{U} \longrightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\mathrm{e} \quad \text{half-life } = 23.5 \text{ min}$$

$$^{239}_{93}\mathrm{Np} \longrightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\mathrm{e} \quad \text{half-life } = 2.36 \text{ days}$$

Plutonium is now mostly formed in nuclear reactors as a byproduct during the fission of U-235. Additional neutrons are released during this fission process (see the next section), some of which combine with U-238 nuclei to form uranium-239; this undergoes β decay to form neptunium-239, which in turn undergoes β decay to form plutonium-239 as illustrated in the preceding three equations. These processes are summarized in the equation:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U} \xrightarrow{\beta^-} {}^{239}_{93}\mathrm{Np} \xrightarrow{\beta^-} {}^{239}_{94}\mathrm{Pu} \tag{18.6.1}$$

Heavier isotopes of plutonium—Pu-240, Pu-241, and Pu-242—are also produced when lighter plutonium nuclei capture neutrons. Some of this highly radioactive plutonium is used to produce military weapons, and the rest presents a serious storage problem because they have half-lives from thousands to hundreds of thousands of years.

Although they have not been prepared in the same quantity as plutonium, many other synthetic nuclei have been produced. Nuclear medicine has developed from the ability to convert atoms of one type into other types of atoms. Radioactive isotopes of several dozen elements are currently used for medical applications. The radiation produced by their decay is used to image or treat various organs or portions of the body, among other uses.

The elements beyond element 92 (uranium) are called **transuranium elements**. As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval. Some of these elements are shown in Table 21.3.

Table 21.3: Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	$^{239}_{94}\text{Pu} + {}^{1}_{0}\text{n} \longrightarrow {}^{240}_{95}\text{Am} + {}^{0}_{-1}\text{e}$
curium	Cm	96	$^{239}_{94}\text{Pu} + {}^{4}_{2}\text{He} \longrightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$
californium	Cf	98	$^{242}_{96}\text{Cm} + {}^{4}_{2}\text{He} \longrightarrow {}^{245}_{98}\text{Cf} + {}^{1}_{0}\text{n}$
einsteinium	Es	99	$^{242}_{96}\text{Cm} + {}^{4}_{2}\text{He} \longrightarrow {}^{245}_{98}\text{Cf} + {}^{1}_{0}\text{n}$
mendelevium	Md	101	$^{253}_{99}\text{Es} + {}^{4}_{2}\text{He} \longrightarrow {}^{256}_{101}\text{Md} + {}^{1}_{0}\text{n}$
nobelium	No	102	$^{246}_{96}\text{Cm} + {}^{12}_{6}\text{C} \longrightarrow {}^{254}_{102}\text{No} + 4{}^{1}_{0}\text{n}$
rutherfordium	Rf	104	$^{249}_{98}\text{Cf} + {}^{12}_{6}\text{C} \longrightarrow {}^{257}_{104}\text{Rf} + 4{}^{1}_{0}\text{n}$ $^{249}_{98}\text{Cf} + {}^{18}_{8}\text{O} \longrightarrow {}^{263}_{106}\text{Sg} + 4{}^{1}_{0}\text{n}$
seaborgium	Sg	106	$^{206}_{82}\text{Pb} + {}^{54}_{24}\text{Cr} \longrightarrow {}^{257}_{106}\text{Sg} + 3{}^{1}_{0}\text{n}$
meitnerium	Mt	107	$^{209}_{83}\text{Bi} + {}^{58}_{26}\text{Fe} \longrightarrow {}^{266}_{109}\text{Mt} + {}^{1}_{0}\text{n}$

Nuclear Fission

Many heavier elements with smaller binding energies per nucleon can decompose into more stable elements that have intermediate mass numbers and larger binding energies per nucleon—that is, mass numbers and binding energies per nucleon that are closer to the "peak" of the binding energy graph near 56 (see Figure 21.3). Sometimes neutrons are also produced. This decomposition is called fission, the breaking of a large nucleus into smaller pieces. The breaking is rather random with the formation of a large number of different products. Fission usually does not occur naturally, but is induced by bombardment with neutrons. The first reported nuclear fission occurred in 1939 when three German scientists, Lise Meitner, Otto Hahn, and Fritz Strassman, bombarded uranium-235 atoms with slow-moving neutrons that split the U-238 nuclei into smaller fragments that consisted of several neutrons and elements near the middle of the periodic table. Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure 18.6.2

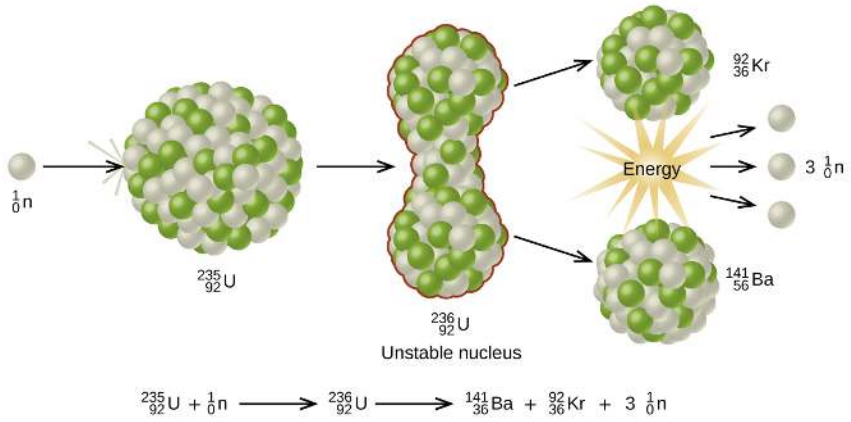


Figure 18.6.2: When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances. A few of the many reactions that occur for U-235, and a graph showing the distribution of its fission products and their yields, are shown in Figure 18.6.3 Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{90}_{38}Sr + {}^{144}_{54}Xe + 2\ {}^{1}_{0}n$

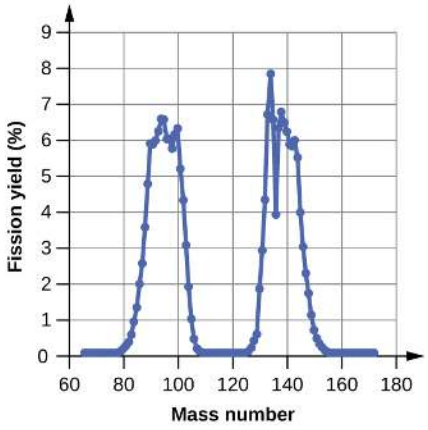
$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{87}_{35}Br + {}^{146}_{57}La + 3\ {}^{1}_{0}n$

$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{96}_{37}Rb + {}^{137}_{55}Cs + 3\ {}^{1}_{0}n$

$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{137}_{52}Te + {}^{97}_{40}Zr + 2\ {}^{1}_{0}n$

$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3\ {}^{1}_{0}n$

(a)



(b)

Figure 18.6.3: (a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

Link to Learning

View this link to see a simulation of nuclear fission.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this "lost" mass is converted into a very large amount of energy, about $1.8\ 10^{10}$ kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

As described earlier, when undergoing fission U-235 produces two "medium-sized" nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear **chain reaction** (see Figure 18.6.4). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

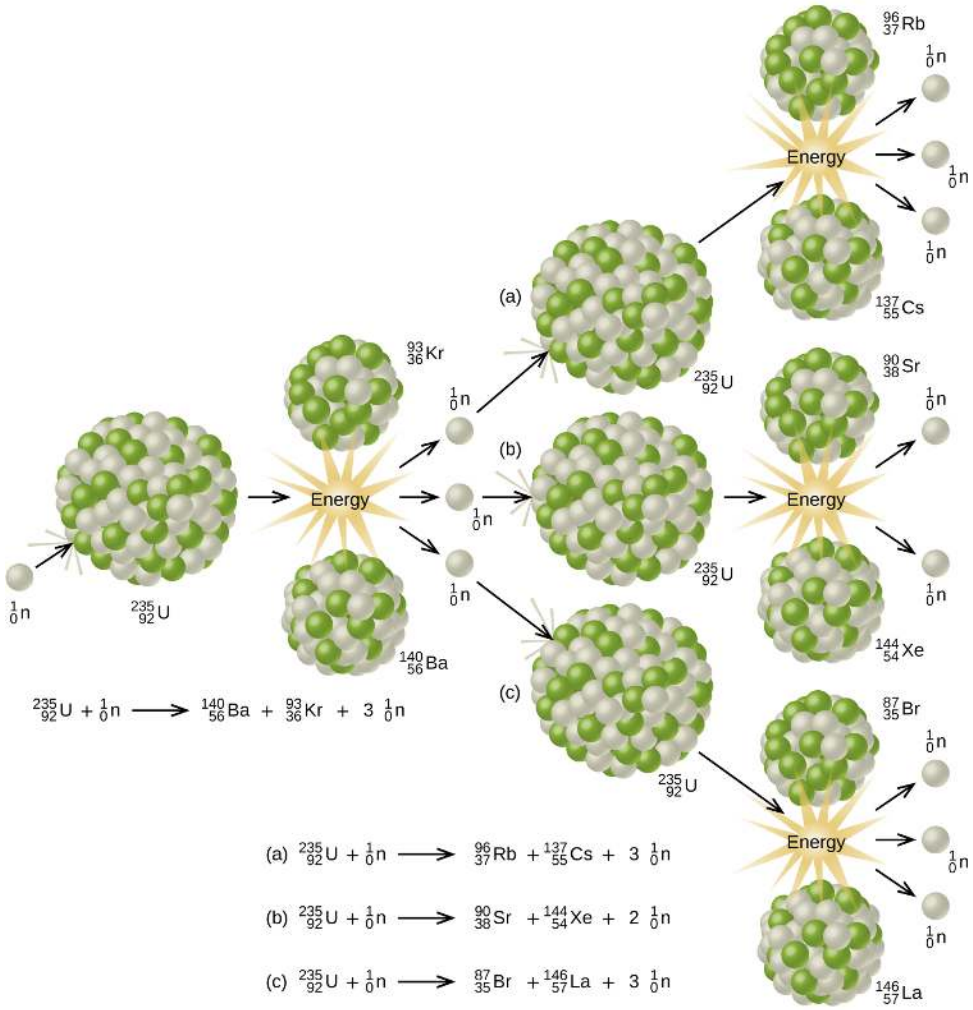


Figure 18.6.4: The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

Material that can sustain a nuclear fission chain reaction is said to be **fissile** or **fissionable**. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a **critical mass**. An amount of fissionable material that cannot sustain a chain reaction is a **subcritical mass**. An amount of material in which there is an increasing rate of fission is known as a **supercritical mass**. The critical mass depends on the type of material: its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled (Figure 18.6.5).

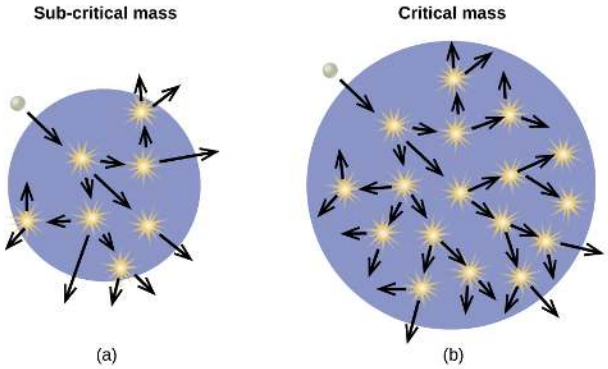


Figure 18.6.5: (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

An atomic bomb (Figure 18.6.6) contains several pounds of fissionable material, $^{235}_{92}\text{U}$ or $^{239}_{94}\text{Pu}$ a source of neutrons, and an explosive device for compressing it quickly into a small volume. When fissionable material is in small pieces, the proportion of neutrons that escape through the relatively large surface area is great, and a chain reaction does not take place. When the small pieces of fissionable material are brought together quickly to form a body with a mass larger than the critical mass, the relative number of escaping neutrons decreases, and a chain reaction and explosion result.

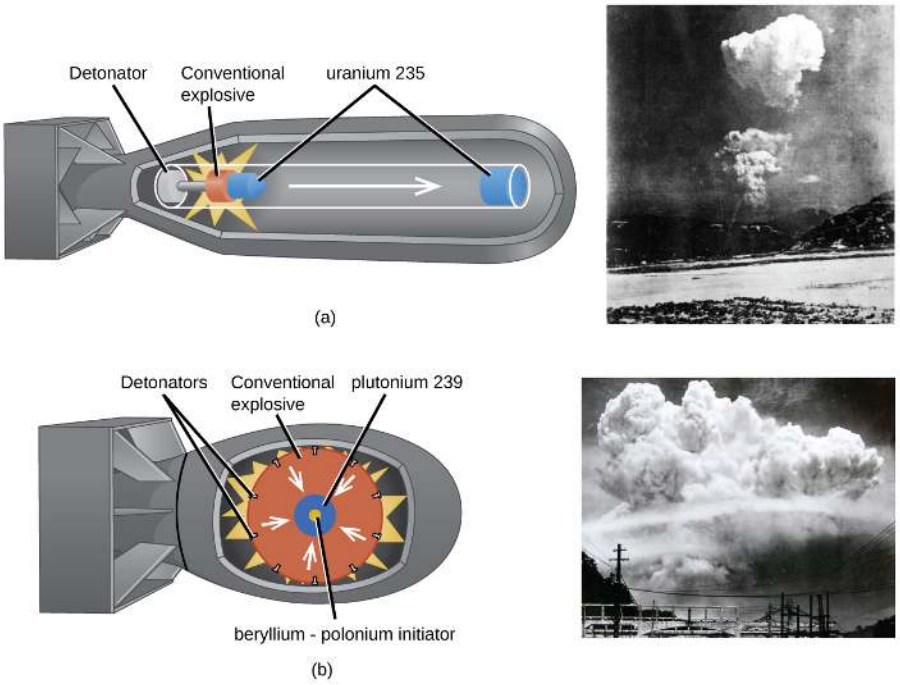


Figure 18.6.6: (a) The nuclear fission bomb that destroyed Hiroshima on August 6, 1945, consisted of two subcritical masses of U-235, where conventional explosives were used to fire one of the subcritical masses into the other, creating the critical mass for the nuclear explosion. (b) The plutonium bomb that destroyed Nagasaki on August 9, 1945, consisted of a hollow sphere of plutonium that was rapidly compressed by conventional explosives. This led to a concentration of plutonium in the center that was greater than the critical mass necessary for the nuclear explosion.

Fission Reactors

Chain reactions of fissionable materials can be controlled and sustained without an explosion in a **nuclear reactor** (Figure 18.6.7). Any nuclear reactor that produces power via the fission of uranium or plutonium by bombardment with neutrons must have at least five components: nuclear fuel consisting of fissionable material, a nuclear moderator, reactor coolant, control rods, and a shield and containment system. We will discuss these components in greater detail later in the section. The reactor works by separating the fissionable nuclear material such that a critical mass cannot be formed, controlling both the flux and absorption of neutrons to allow shutting down the fission reactions. In a nuclear reactor used for the production of electricity, the energy released by fission

reactions is trapped as thermal energy and used to boil water and produce steam. The steam is used to turn a turbine, which powers a generator for the production of electricity.

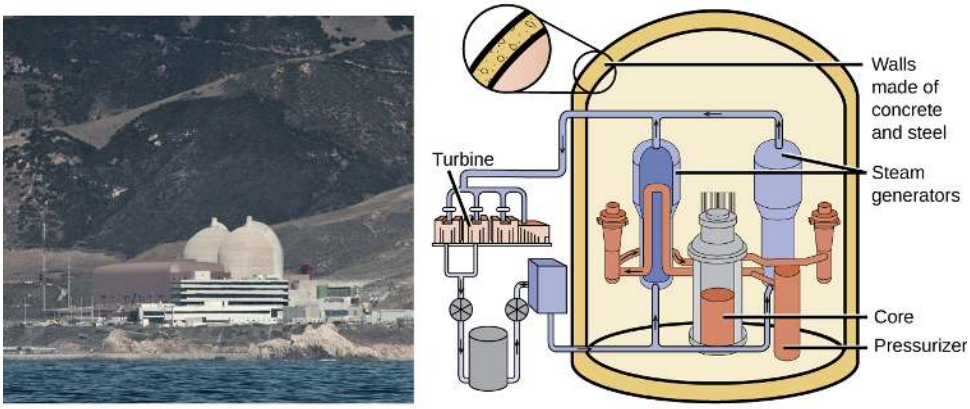


Figure 18.6.7: (a) The Diablo Canyon Nuclear Power Plant near San Luis Obispo is the only nuclear power plant currently in operation in California. The domes are the containment structures for the nuclear reactors, and the brown building houses the turbine where electricity is generated. Ocean water is used for cooling. (b) The Diablo Canyon uses a pressurized water reactor, one of a few different fission reactor designs in use around the world, to produce electricity. Energy from the nuclear fission reactions in the core heats water in a closed, pressurized system. Heat from this system produces steam that drives a turbine, which in turn produces electricity. (credit a: modification of work by “Mike” Michael L. Baird; credit b: modification of work by the Nuclear Regulatory Commission)

Nuclear Fuels

Nuclear fuel consists of a fissionable isotope, such as uranium-235, which must be present in sufficient quantity to provide a self-sustaining chain reaction. In the United States, uranium ores contain from 0.05–0.3% of the uranium oxide U_3O_8; the uranium in the ore is about 99.3% nonfissionable U-238 with only 0.7% fissionable U-235. Nuclear reactors require a fuel with a higher concentration of U-235 than is found in nature; it is normally enriched to have about 5% of uranium mass as U-235. At this concentration, it is not possible to achieve the supercritical mass necessary for a nuclear explosion. Uranium can be enriched by gaseous diffusion (the only method currently used in the US), using a gas centrifuge, or by laser separation.

In the gaseous diffusion enrichment plant where U-235 fuel is prepared, UF_6 (uranium hexafluoride) gas at low pressure moves through barriers that have holes just barely large enough for UF_6 to pass through. The slightly lighter $^{235}UF_6$ molecules diffuse through the barrier slightly faster than the heavier $^{238}UF_6$ molecules. This process is repeated through hundreds of barriers, gradually increasing the concentration of $^{235}UF_6$ to the level needed by the nuclear reactor. The basis for this process, Graham’s law, is described in the chapter on gases. The enriched UF_6 gas is collected, cooled until it solidifies, and then taken to a fabrication facility where it is made into fuel assemblies. Each fuel assembly consists of fuel rods that contain many thimble-sized, ceramic-encased, enriched uranium (usually UO_2) fuel pellets. Modern nuclear reactors may contain as many as 10 million fuel pellets. The amount of energy in each of these pellets is equal to that in almost a ton of coal or 150 gallons of oil.

Nuclear Moderators

Neutrons produced by nuclear reactions move too fast to cause fission (refer back to Figure 18.6.5). They must first be slowed to be absorbed by the fuel and produce additional nuclear reactions. A **nuclear moderator** is a substance that slows the neutrons to a speed that is low enough to cause fission. Early reactors used high-purity graphite as a moderator. Modern reactors in the US exclusively use heavy water or light water (ordinary H_2O), whereas some reactors in other countries use other materials, such as carbon dioxide, beryllium, or graphite.

Reactor Coolants

A nuclear reactor coolant is used to carry the heat produced by the fission reaction to an external boiler and turbine, where it is transformed into electricity. Two overlapping coolant loops are often used; this counteracts the transfer of radioactivity from the reactor to the primary coolant loop. All nuclear power plants in the US use water as a coolant. Other coolants include molten sodium, lead, a lead-bismuth mixture, or molten salts.

Control Rods

Nuclear reactors use control rods (Figure 18.6.8) to control the fission rate of the nuclear fuel by adjusting the number of slow neutrons present to keep the rate of the chain reaction at a safe level. Control rods are made of boron, cadmium, hafnium, or other elements that are able to absorb neutrons. Boron-10, for example, absorbs neutrons by a reaction that produces lithium-7 and alpha particles:

$$^{10}_{5}\mathrm{B} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{7}_{3}\mathrm{Li} + {}^{4}_{2}\mathrm{He} \tag{18.6.2}$$

When control rod assemblies are inserted into the fuel element in the reactor core, they absorb a larger fraction of the slow neutrons, thereby slowing the rate of the fission reaction and decreasing the power produced. Conversely, if the control rods are removed, fewer neutrons are absorbed, and the fission rate and energy production increase. In an emergency, the chain reaction can be shut down by fully inserting all of the control rods into the nuclear core between the fuel rods.

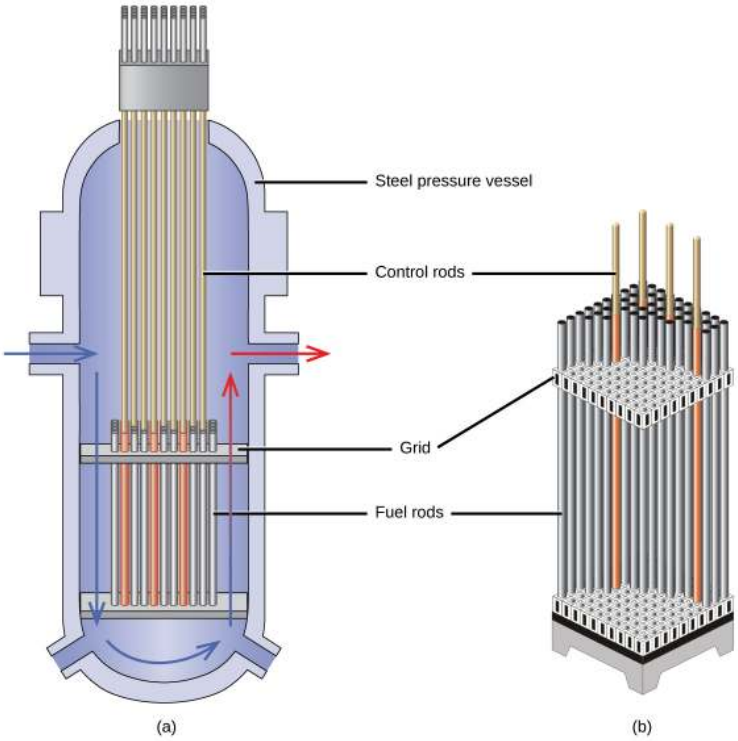


Figure 18.6.8: The nuclear reactor core shown in (a) contains the fuel and control rod assembly shown in (b). (credit: modification of work by E. Generalic, http://glossary.periodni.com/glossar...en=control+rod)

Shield and Containment System

During its operation, a nuclear reactor produces neutrons and other radiation. Even when shut down, the decay products are radioactive. In addition, an operating reactor is thermally very hot, and high pressures result from the circulation of water or another coolant through it. Thus, a reactor must withstand high temperatures and pressures, and must protect operating personnel from the radiation. Reactors are equipped with a **containment system** (or shield) that consists of three parts:

1. The reactor vessel, a steel shell that is 3–20-centimeters thick and, with the moderator, absorbs much of the radiation produced by the reactor
2. A main shield of 1–3 meters of high-density concrete
3. A personnel shield of lighter materials that protects operators from γ rays and X-rays

In addition, reactors are often covered with a steel or concrete dome that is designed to contain any radioactive materials might be released by a reactor accident.

Link to Learning

Click here to watch a 3-minute video from the Nuclear Energy Institute on how nuclear reactors work.

Nuclear power plants are designed in such a way that they cannot form a supercritical mass of fissionable material and therefore cannot create a nuclear explosion. But as history has shown, failures of systems and safeguards can cause catastrophic accidents, including chemical explosions and nuclear meltdowns (damage to the reactor core from overheating). The following Chemistry in Everyday Life feature explores three infamous meltdown incidents.

Chemistry in Everyday Life: Nuclear Accidents

The importance of cooling and containment are amply illustrated by three major accidents that occurred with the nuclear reactors at nuclear power generating stations in the United States (Three Mile Island), the former Soviet Union (Chernobyl), and Japan (Fukushima).

In March 1979, the cooling system of the Unit 2 reactor at Three Mile Island Nuclear Generating Station in Pennsylvania failed, and the cooling water spilled from the reactor onto the floor of the containment building. After the pumps stopped, the reactors overheated due to the high radioactive decay heat produced in the first few days after the nuclear reactor shut down. The temperature of the core climbed to at least 2200 °C, and the upper portion of the core began to melt. In addition, the zirconium alloy cladding of the fuel rods began to react with steam and produced hydrogen:

$$\mathrm{Zr(s) + 2\,H_2O(g) \longrightarrow ZrO_2(s) + 2\,H_2(g)}$$

The hydrogen accumulated in the confinement building, and it was feared that there was danger of an explosion of the mixture of hydrogen and air in the building. Consequently, hydrogen gas and radioactive gases (primarily krypton and xenon) were vented from the building. Within a week, cooling water circulation was restored and the core began to cool. The plant was closed for nearly 10 years during the cleanup process.

Although zero discharge of radioactive material is desirable, the discharge of radioactive krypton and xenon, such as occurred at the Three Mile Island plant, is among the most tolerable. These gases readily disperse in the atmosphere and thus do not produce highly radioactive areas. Moreover, they are noble gases and are not incorporated into plant and animal matter in the food chain. Effectively none of the heavy elements of the core of the reactor were released into the environment, and no cleanup of the area outside of the containment building was necessary (Figure 18.6.9).

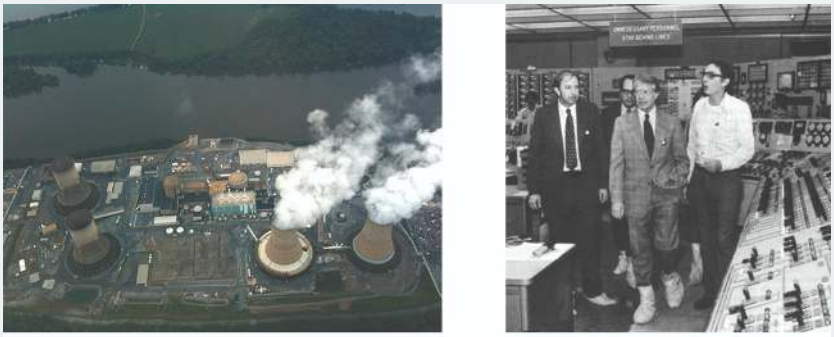


Figure 18.6.9: (a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control room a few days after the accident in 1979.

Another major nuclear accident involving a reactor occurred in April 1986, at the Chernobyl Nuclear Power Plant in Ukraine, which was still a part of the former Soviet Union. While operating at low power during an unauthorized experiment with some of its safety devices shut off, one of the reactors at the plant became unstable. Its chain reaction became uncontrollable and increased to a level far beyond what the reactor was designed for. The steam pressure in the reactor rose to between 100 and 500 times the full power pressure and ruptured the reactor. Because the reactor was not enclosed in a containment building, a large amount of radioactive material spewed out, and additional fission products were released, as the graphite (carbon) moderator of the core ignited and burned. The fire was controlled, but over 200 plant workers and firefighters developed acute radiation sickness and at least 32 soon died from the effects of the radiation. It is predicted that about 4000 more deaths will

occur among emergency workers and former Chernobyl residents from radiation-induced cancer and leukemia. The reactor has since been encapsulated in steel and concrete, a now-decaying structure known as the sarcophagus. Almost 30 years later, significant radiation problems still persist in the area, and Chernobyl largely remains a wasteland.

In 2011, the Fukushima Daiichi Nuclear Power Plant in Japan was badly damaged by a 9.0-magnitude earthquake and resulting tsunami. Three reactors up and running at the time were shut down automatically, and emergency generators came online to power electronics and coolant systems. However, the tsunami quickly flooded the emergency generators and cut power to the pumps that circulated coolant water through the reactors. High-temperature steam in the reactors reacted with zirconium alloy to produce hydrogen gas. The gas escaped into the containment building, and the mixture of hydrogen and air exploded. Radioactive material was released from the containment vessels as the result of deliberate venting to reduce the hydrogen pressure, deliberate discharge of coolant water into the sea, and accidental or uncontrolled events.

An evacuation zone around the damaged plant extended over 12.4 miles away, and an estimated 200,000 people were evacuated from the area. All 48 of Japan's nuclear power plants were subsequently shut down, remaining shuttered as of December 2014. Since the disaster, public opinion has shifted from largely favoring to largely opposing increasing the use of nuclear power plants, and a restart of Japan's atomic energy program is still stalled (Figure 18.6.10).



Figure 18.6.10: (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by "Live Action Hero"/Flickr)

The energy produced by a reactor fueled with enriched uranium results from the fission of uranium as well as from the fission of plutonium produced as the reactor operates. As discussed previously, the plutonium forms from the combination of neutrons and the uranium in the fuel. In any nuclear reactor, only about 0.1% of the mass of the fuel is converted into energy. The other 99.9% remains in the fuel rods as fission products and unused fuel. All of the fission products absorb neutrons, and after a period of several months to a few years, depending on the reactor, the fission products must be removed by changing the fuel rods. Otherwise, the concentration of these fission products would increase and absorb more neutrons until the reactor could no longer operate.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

Link to Learning

Explore the information in this link to learn about the approaches to nuclear waste management.

Nuclear Fusion and Fusion Reactors

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called fusion. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse

and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{+1}\mathrm{e}^{+}$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about 3.6 10^{11} kJ of energy per mole of \({ }_2^4 \mathrm{He}\) produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 (1.8 10^{10} kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

It has been determined that the nuclei of the heavy isotopes of hydrogen, a deuteron, ${}^{2}_{1}\mathrm{H}$, and a triton, ${}^{3}_{1}\mathrm{H}$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$$ {}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} \tag{18.6.3}$$

This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69 10^{9} kilojoules per mole of \({ }_2^4 \mathrm{He}\) formed. The very high temperature is necessary to give the nuclei enough kinetic energy to overcome the very strong repulsive forces resulting from the positive charges on their nuclei so they can collide.

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.

Another much more beneficial way to create fusion reactions is in a **fusion reactor**, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure 18.6.11). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. At the time of this writing, there are no self-sustaining fusion reactors operating in the world, although small-scale controlled fusion reactions have been run for very brief periods.

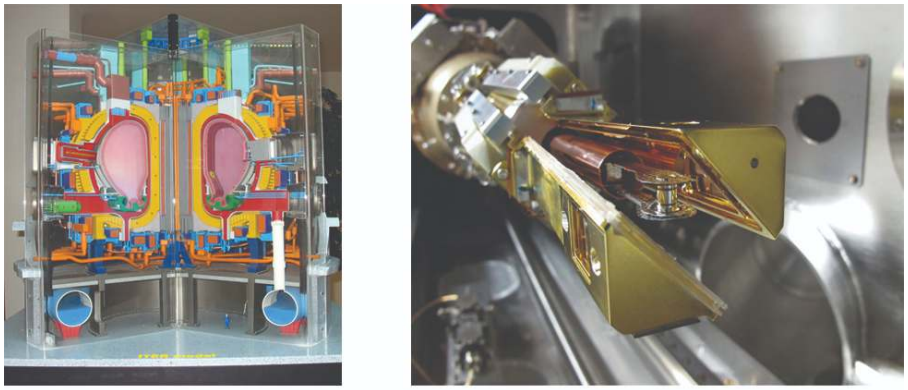


Figure 18.6.11: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving large-scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

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18.7: Uses of Radioisotopes

Learning Objectives

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

- List common applications of radioactive isotopes

Radioactive isotopes have the same chemical properties as stable isotopes of the same element, but they emit radiation, which can be detected. If we replace one (or more) atom(s) with radioisotope(s) in a compound, we can track them by monitoring their radioactive emissions. This type of compound is called a radioactive tracer (or radioactive label). Radioisotopes are used to follow the paths of biochemical reactions or to determine how a substance is distributed within an organism. Radioactive tracers are also used in many medical applications, including both diagnosis and treatment. They are used to measure engine wear, analyze the geological formation around oil wells, and much more.

Radioimmunossays (RIA), for example, rely on radioisotopes to detect the presence and/or concentration of certain antigens. Developed by Rosalyn Sussman Yalow and Solomon Berson in the 1950s, the technique is known for extreme sensitivity, meaning that it can detect and measure very small quantities of a substance. Prior to its discovery, most similar detection relied on large enough quantities to produce visible outcomes. RIA revolutionized and expanded entire fields of study, most notably endocrinology, and is commonly used in narcotics detection, blood bank screening, early cancer screening, hormone measurement, and allergy diagnosis. Based on her significant contribution to medicine, Yalow received a Nobel Prize, making her the second woman to be awarded the prize for medicine.

Radioisotopes have revolutionized medical practice (see Appendix M), where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States. Four typical examples of radioactive tracers used in medicine are technetium-99 ($^{99}_{43}\mathrm{Tc}$), thallium-201 ($^{201}_{81}\mathrm{Tl}$), iodine-131 ($^{131}_{53}\mathrm{I}$), and sodium-24 ($^{24}_{11}\mathrm{Na}$). Damaged tissues in the heart, liver, and lungs absorb certain compounds of technetium-99 preferentially. After it is injected, the location of the technetium compound, and hence the damaged tissue, can be determined by detecting the γ rays emitted by the Tc-99 isotope. Thallium-201 (Figure 18.7.1) becomes concentrated in healthy heart tissue, so the two isotopes, Tc-99 and Tl-201, are used together to study heart tissue. Iodine-131 concentrates in the thyroid gland, the liver, and some parts of the brain. It can therefore be used to monitor goiter and treat thyroid conditions, such as Grave's disease, as well as liver and brain tumors. Salt solutions containing compounds of sodium-24 are injected into the bloodstream to help locate obstructions to the flow of blood.

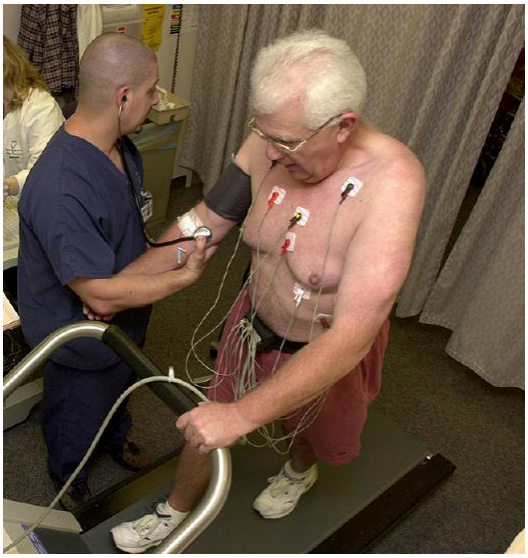


Figure 18.7.1: Administering thallium-201 to a patient and subsequently performing a stress test offer medical professionals an opportunity to visually analyze heart function and blood flow. (credit: modification of work by "Blue0ctane"/Wikimedia Commons)

Radioisotopes used in medicine typically have short half-lives—for example, the ubiquitous Tc-99m has a half-life of 6.01 hours. This makes Tc-99m essentially impossible to store and prohibitively expensive to transport, so it is made on-site instead. Hospitals and other medical facilities use Mo-99 (which is primarily extracted from U-235 fission products) to generate Tc-99. Mo-99 undergoes β decay with a half-life of 66 hours, and the Tc-99 is then chemically extracted (Figure 18.7.2). The parent nuclide Mo-99 is part of a molybdate ion, MoO_4^{2-}; when it decays, it forms the pertechnetate ion, TcO_4^-. These two water-soluble ions are separated by column chromatography, with the higher charge molybdate ion adsorbing onto the alumina in the column, and the lower charge pertechnetate ion passing through the column in the solution. A few micrograms of Mo-99 can produce enough Tc-99 to perform as many as 10,000 tests.

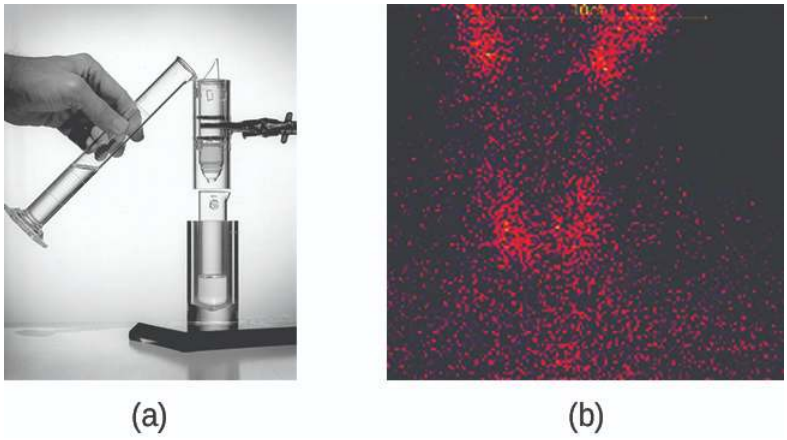


Figure 18.7.2: (a) The first Tc-99m generator (circa 1958) is used to separate Tc-99 from Mo-99. The is retained by the matrix in the column, whereas the passes through and is collected. (b) Tc-99 was used in this scan of the neck of a patient with Grave's disease. The scan shows the location of high concentrations of Tc-99. (credit a: modification of work by the Department of Energy; credit b: modification of work by "MBq"/Wikimedia Commons)

Radioisotopes can also be used, typically in higher doses than as a tracer, as treatment. Radiation therapy is the use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing (Figure 18.7.3). A cancer patient may receive external beam radiation therapy delivered by a machine outside the body, or internal radiation therapy (brachytherapy) from a radioactive substance that has been introduced into the body. Note that chemotherapy is similar to internal radiation therapy in that the cancer treatment is injected into the body, but differs in that chemotherapy uses chemical rather than radioactive substances to kill the cancer cells.

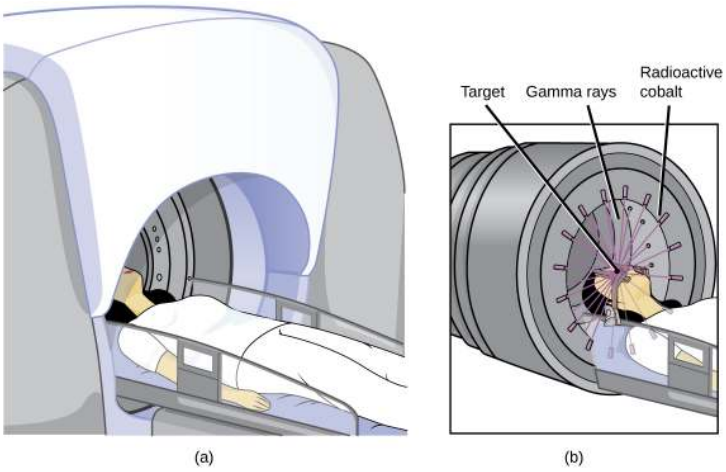


Figure 18.7.3: The cartoon in (a) shows a coba machine swings through an arc, focusing radiation on the targeted region (tumor) and minimizing the amount of radiation that passes through nearby regions.

Cobalt-60 is a synthetic radioisotope produced by the neutron activation of Co-59, which then undergoes β decay to form Ni-60, along with the emission of γ radiation. The overall process is:

$$^{59}_{27}\mathrm{Co} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{60}_{27}\mathrm{Co} \rightarrow {}^{60}_{28}\mathrm{Ni} + {}^{0}_{-1}\beta + 2{}^{0}_{0}\gamma \tag{18.7.1}$$

The overall decay scheme for this is shown graphically in Figure 18.7.4

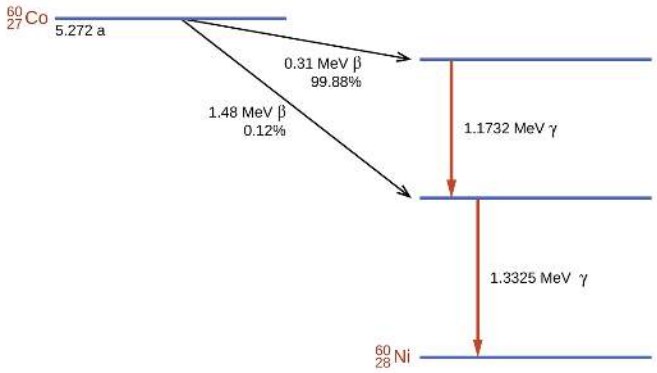


Figure 18.7.4: Co-60 undergoes a series of radioactive decays. The γ emissions are used for radiation therapy.

Radioisotopes are used in diverse ways to study the mechanisms of chemical reactions in plants and animals. These include labeling fertilizers in studies of nutrient uptake by plants and crop growth, investigations of digestive and milk-producing processes in cows, and studies on the growth and metabolism of animals and plants.

For example, the radioisotope C-14 was used to elucidate the details of how photosynthesis occurs. The overall reaction is:

$$6CO_2(g) + 6H_2O\ (l) \rightarrow C_6H_{12}O_6\ (s) + 6O_2\ (g), \tag{18.7.2}$$

but the process is much more complex, proceeding through a series of steps in which various organic compounds are produced. In studies of the pathway of this reaction, plants were exposed to CO_2 containing a high concentration of ($^{14}_{6}C$). At regular intervals, the plants were analyzed to determine which organic compounds contained carbon-14 and how much of each compound was present. From the time sequence in which the compounds appeared and the amount of each present at given time intervals, scientists learned more about the pathway of the reaction.

Commercial applications of radioactive materials are equally diverse (Figure 18.7.5). They include determining the thickness of films and thin metal sheets by exploiting the penetration power of various types of radiation. Flaws in metals used for structural purposes can be detected using high-energy gamma rays from cobalt-60 in a fashion similar to the way X-rays are used to examine the human body. In one form of pest control, flies are controlled by sterilizing male flies with γ radiation so that females breeding with them do not produce offspring. Many foods are preserved by radiation that kills microorganisms that cause the foods to spoil.



Figure 18.7.5: Common commercial uses of radiation include (a) X-ray examination of luggage at an airport and (b) preservation of food. (credit a: modification of work by the Department of the Navy; credit b: modification of work by the US Department of Agriculture)

Americium-241, an α emitter with a half-life of 458 years, is used in tiny amounts in ionization-type smoke detectors (Figure 18.7.6). The α emissions from Am-241 ionize the air between two electrode plates in the ionizing chamber. A battery supplies a potential that causes movement of the ions, thus creating a small electric current. When smoke enters the chamber, the movement of the ions is impeded, reducing the conductivity of the air. This causes a marked drop in the current, triggering an alarm.

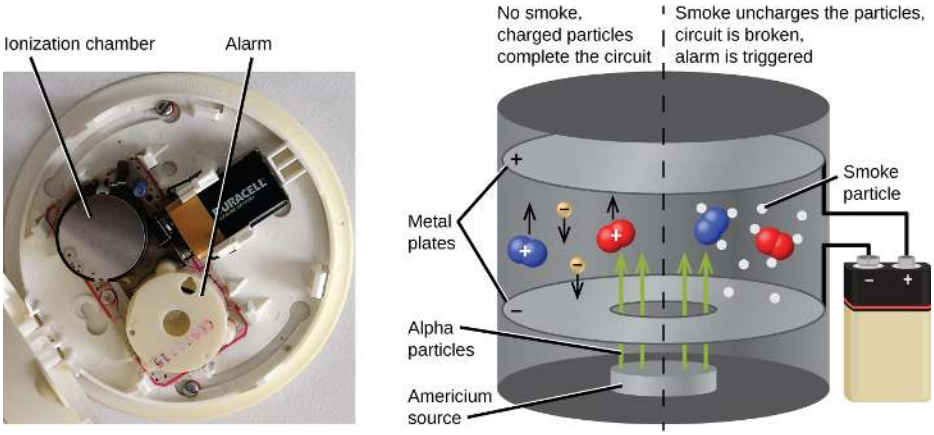


Figure 18.7.6: Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by "Muffet"/Wikimedia Commons)

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18.8: Biological Effects of Radiation

Learning Objectives

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

- Describe the biological impact of ionizing radiation
- Define units for measuring radiation exposure
- Explain the operation of common tools for detecting radioactivity
- List common sources of radiation exposure in the US

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure 18.8.1).

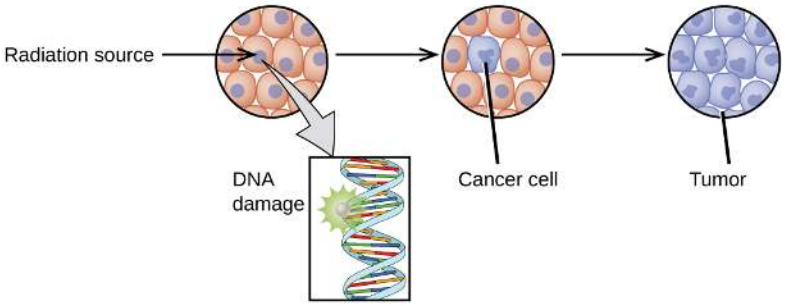


Figure 18.8.1: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

Ionizing and Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure 18.8.2).

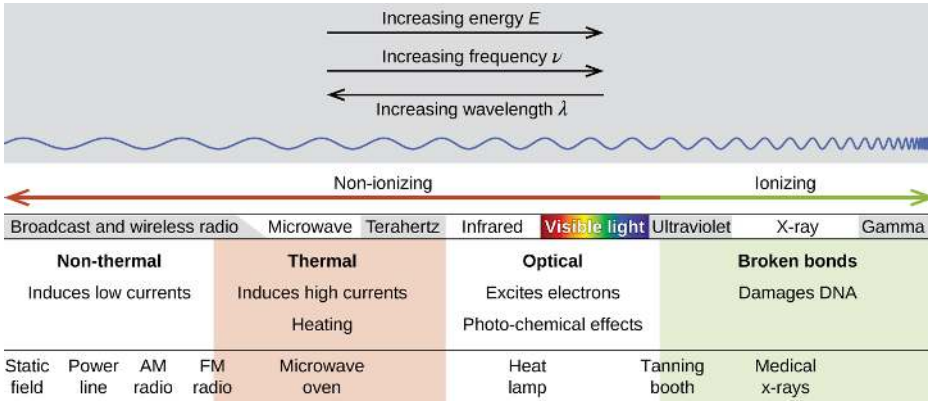


Figure 18.8.2: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation,

however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

$$H_2O + \text{radiation} \xrightarrow{e^-} H_2O^+ + H_2O \longrightarrow H_3O^+ + OH^\bullet$$

Because the hydroxyl radical has an unpaired electron, it is highly reactive. (This is true of any substance with unpaired electrons, known as a free radical.) This hydroxyl radical can react with all kinds of biological molecules (DNA, proteins, enzymes, and so on), causing damage to the molecules and disrupting physiological processes. Examples of direct and indirect damage are shown in Figure 21.32.

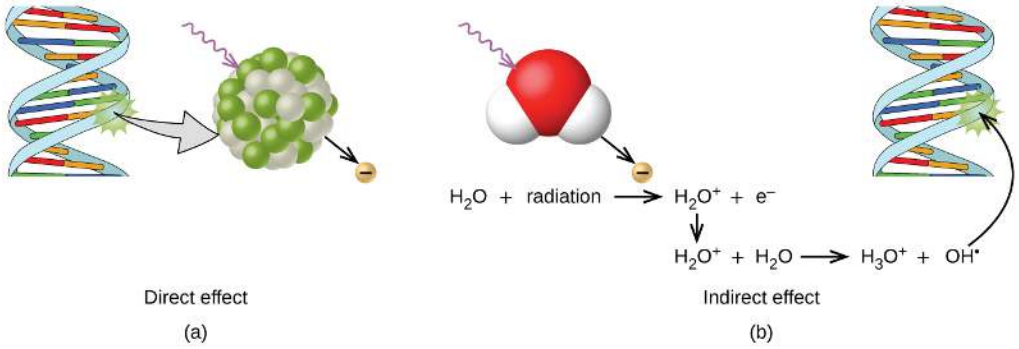


Figure 21.32 Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material (Figure 18.8.3). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.

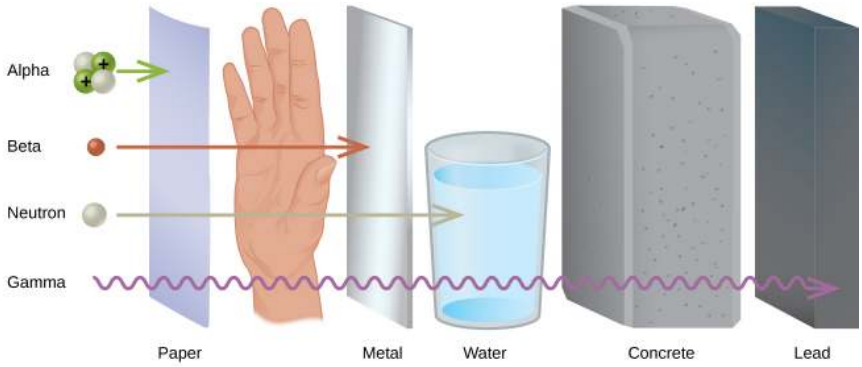


Figure 18.8.3: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.

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Chemistry in Everyday Life: Radon Exposure

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238 (Figure 21.9), which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure 18.8.4).

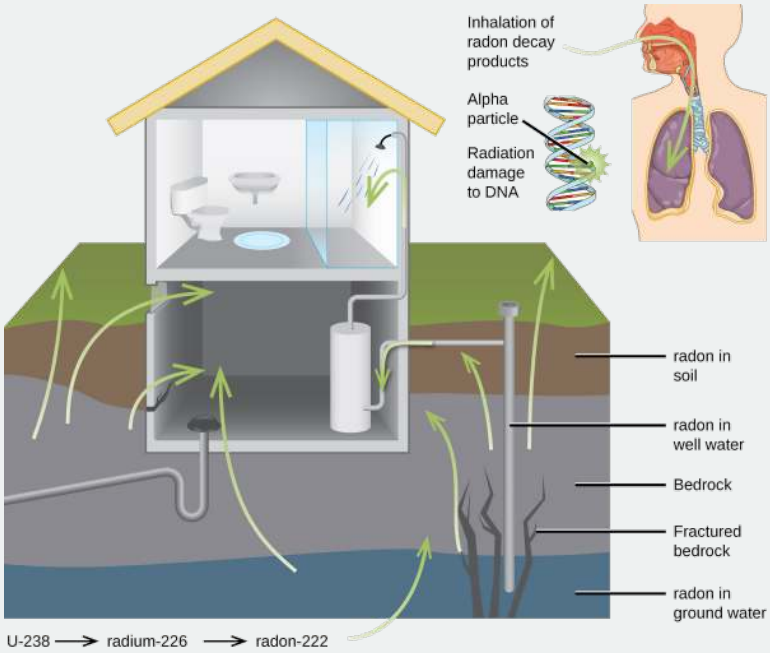


Figure 18.8.4: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

Radon is found in buildings across the country, with amounts depending on where you live. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the levels found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure 18.8.5). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.

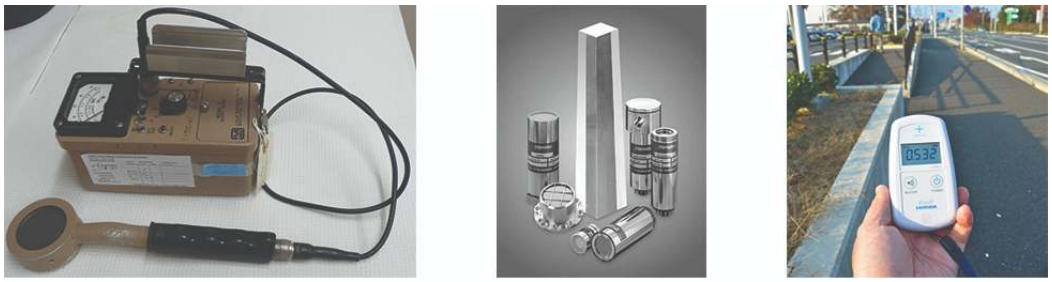


Figure 18.8.5: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (credit c: modification of work by “osaMu”/Wikimedia commons)

A variety of units are used to measure various aspects of radiation (Figure 18.8.6). The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = 3.7 10^{10} disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose. The roentgen equivalent for man (rem) is the unit for radiation damage that is used most frequently in medicine (100 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy) along with a biological factor referred to as the RBE (for relative biological effectiveness) that is an approximate measure of the relative damage done by the radiation. These are related by:

$$\text{number of rems} = \text{RBE} \times \text{number of rads} \tag{18.8.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

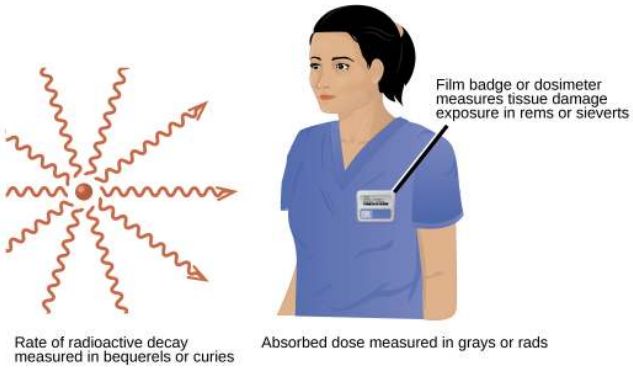


Figure 18.8.6: Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does.

Units of Radiation Measurement

Table 18.8.1 summarizes the units used for measuring radiation.

Table 18.8.1: Units Used for Measuring Radiation

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes 3.7 10^{10} decays/second
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue

Measurement Purpose	Unit	Quantity Measured	Description
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE Gy
	roentgen equivalent for man (rem)		Rem = RBE rad

Example 18.8.1: Amount of Radiation

Cobalt-60 ($t_{1/2} = 5.26\ y$) is used in cancer therapy since the γ rays it emits can be focused in small areas where the cancer is located. A 5.00-g sample of Co-60 is available for cancer treatment.

a. What is its activity in Bq?
b. What is its activity in Ci?

Solution

The activity is given by:

$$\text{Activity } = \lambda N = \left(\frac{\ln 2}{t_{1/2}}\right) N = \left(\frac{\ln 2}{5.26\text{y}}\right) \times 5.00\text{ g} = 0.659 \frac{\text{g}}{\text{y}} \text{ of Co } -60 \text{ that decay}$$

And to convert this to decays per second:

$$0.659 \frac{\text{g}}{\text{y}} \times \frac{1\text{y}}{365\text{ d}} \times \frac{1\text{ d}}{24\text{ h}} \times \frac{1\text{ h}}{3600\text{ s}} \times \frac{1\text{ mol}}{59.9\text{ g}} \times \frac{6.02 \times 10^{23}\text{ atoms}}{1\text{ mol}} \times \frac{1\text{ decay}}{1\text{ atom}}$$
$$= 2.10 \times 10^{14} \frac{\text{decay}}{\text{s}}$$

a. Since $1\text{ Bq} = \frac{1\text{ decay}}{\text{s}}$ the activity in Becquerel (Bq) is:

$$2.10 \times 10^{14} \frac{\text{decay}}{\text{s}} \times \left(\frac{1\text{ Bq}}{1 \frac{\text{decay}}{\text{s}}}\right) = 2.10 \times 10^{14}\text{ Bq}$$

b. Since $1\text{Ci} = \frac{3.7 \times 10^{11}\text{ decay}}{\text{s}}$ the activity in curie (Ci) is:

$$2.10 \times 10^{14} \frac{\text{decay}}{\text{s}} \times \left(\frac{1\text{Ci}}{\frac{3.7 \times 10^{11}\text{ decay}}{\text{s}}}\right) = 5.7 \times 10^{2}\text{Ci}$$

Exercise 18.8.1

Tritium is a radioactive isotope of hydrogen ($t_{1/2}$ = 12.32 y) that has several uses, including self-powered lighting, in which electrons emitted in tritium radioactive decay cause phosphorus to glow. Its nucleus contains one proton and two neutrons, and the atomic mass of tritium is 3.016 amu. What is the activity of a sample containing 1.00mg of tritium (a) in Bq and (b) in Ci?

Answer

a. 3.56 10^{11} Bq;
b. 0.962 Ci

Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure 18.8.7: , the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer

products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

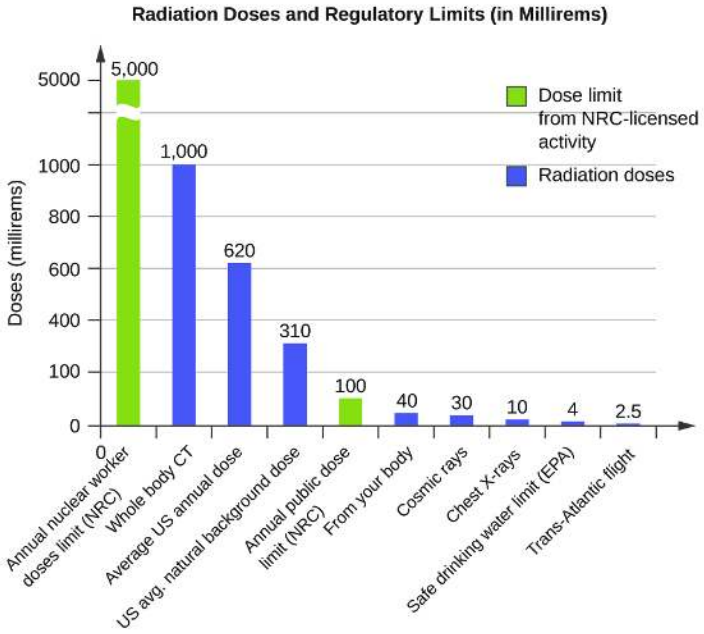


Figure 18.8.7: The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission)

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person's lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table 18.8.2

Table 18.8.2: Health Effects of Radiation[2]

Exposure (rem)	Health Effect	Time to Onset (without treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness;	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

Footnotes

- 2Source: US Environmental Protection Agency

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18.9: Key Terms

alpha (α) decay | loss of an alpha particle during radioactive decay

alpha particle | (α or or high-energy helium nucleus; a helium atom that has lost two electrons and contains two protons and two neutrons

antimatter | particles with the same mass but opposite properties (such as charge) of ordinary particles

band of stability | (also, belt of stability, zone of stability, or valley of stability) region of graph of number of protons versus number of neutrons containing stable (nonradioactive) nuclides

becquerel (Bq) | SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s

beta (β) decay | breakdown of a neutron into a proton, which remains in the nucleus, and an electron, which is emitted as a beta particle

beta particle | or or high-energy electron

binding energy per nucleon | total binding energy for the nucleus divided by the number of nucleons in the nucleus

chain reaction | repeated fission caused when the neutrons released in fission bombard other atoms

chemotherapy | similar to internal radiation therapy, but chemical rather than radioactive substances are introduced into the body to kill cancer cells

containment system | (also, shield) a three-part structure of materials that protects the exterior of a nuclear fission reactor and operating personnel from the high temperatures, pressures, and radiation levels inside the reactor

control rod | material inserted into the fuel assembly that absorbs neutrons and can be raised or lowered to adjust the rate of a fission reaction

critical mass | amount of fissionable material that will support a self-sustaining (nuclear fission) chain reaction

curie (Ci) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7 10^{10} disintegrations/s

daughter nuclide | nuclide produced by the radioactive decay of another nuclide; may be stable or may decay further

electron capture | combination of a core electron with a proton to yield a neutron within the nucleus

electron volt (eV) | measurement unit of nuclear binding energies, with 1 eV equaling the amount energy due to the moving an electron across an electric potential difference of 1 volt

external beam radiation therapy | radiation delivered by a machine outside the body

fissile (or fissionable) | when a material is capable of sustaining a nuclear fission reaction

fission | splitting of a heavier nucleus into two or more lighter nuclei, usually accompanied by the conversion of mass into large amounts of energy

fusion | combination of very light nuclei into heavier nuclei, accompanied by the conversion of mass into large amounts of energy

fusion reactor | nuclear reactor in which fusion reactions of light nuclei are controlled

gamma (γ) emission | decay of an excited-state nuclide accompanied by emission of a gamma ray

gamma ray | (γ or short wavelength, high-energy electromagnetic radiation that exhibits wave-particle duality

Geiger counter | instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube

gray (Gy) | SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue

half-life ($t_{1/2}$) | time required for half of the atoms in a radioactive sample to decay

internal radiation therapy | (also, brachytherapy) radiation from a radioactive substance introduced into the body to kill cancer cells

ionizing radiation | radiation that can cause a molecule to lose an electron and form an ion

magic number | nuclei with specific numbers of nucleons that are within the band of stability

mass defect | difference between the mass of an atom and the summed mass of its constituent subatomic particles (or the mass “lost” when nucleons are brought together to form a nucleus)

mass-energy equivalence equation | Albert Einstein’s relationship showing that mass and energy are equivalent

millicurie (mCi) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7 10^{10} disintegrations/s

nonionizing radiation | radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules

nuclear binding energy | energy lost when an atom’s nucleons are bound together (or the energy needed to break a nucleus into its constituent protons and neutrons)

nuclear chemistry | study of the structure of atomic nuclei and processes that change nuclear structure

nuclear fuel | fissionable isotope present in sufficient quantities to provide a self-sustaining chain reaction in a nuclear reactor

nuclear moderator | substance that slows neutrons to a speed low enough to cause fission

nuclear reaction | change to a nucleus resulting in changes in the atomic number, mass number, or energy state

nuclear reactor | environment that produces energy via nuclear fission in which the chain reaction is controlled and sustained without explosion

nuclear transmutation | conversion of one nuclide into another nuclide

nucleon | collective term for protons and neutrons in a nucleus

nuclide | nucleus of a particular isotope

parent nuclide | unstable nuclide that changes spontaneously into another (daughter) nuclide

particle accelerator | device that uses electric and magnetic fields to increase the kinetic energy of nuclei used in transmutation reactions

positron or | antiparticle to the electron; it has identical properties to an electron, except for having the opposite (positive) charge

positron emission | (also, β^+ decay) conversion of a proton into a neutron, which remains in the nucleus, and a positron, which is emitted

radiation absorbed dose (rad) | SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy

radiation dosimeter | device that measures ionizing radiation and is used to determine personal radiation exposure

radiation therapy | use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing

radioactive decay | spontaneous decay of an unstable nuclide into another nuclide

radioactive decay series | chains of successive disintegrations (radioactive decays) that ultimately lead to a stable end-product

radioactive tracer | (also, radioactive label) radioisotope used to track or follow a substance by monitoring its radioactive emissions

radioactivity | phenomenon exhibited by an unstable nucleon that spontaneously undergoes change into a nucleon that is more stable; an unstable nucleon is said to be radioactive

radiocarbon dating | highly accurate means of dating objects 30,000–50,000 years old that were derived from once-living matter; achieved by calculating the ratio of in the object vs. the ratio of in the present-day atmosphere

radioisotope | isotope that is unstable and undergoes conversion into a different, more stable isotope

radiometric dating | use of radioisotopes and their properties to date the formation of objects such as archeological artifacts, formerly living organisms, or geological formations

reactor coolant | assembly used to carry the heat produced by fission in a reactor to an external boiler and turbine where it is transformed into electricity

relative biological effectiveness (RBE) | measure of the relative damage done by radiation

roentgen equivalent man (rem) | unit for radiation damage, frequently used in medicine; 100 rem = 1 Sv

scintillation counter | instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation

sievert (Sv) | SI unit measuring tissue damage caused by radiation; takes into account energy and biological effects of radiation

strong nuclear force | force of attraction between nucleons that holds a nucleus together

subcritical mass | amount of fissionable material that cannot sustain a chain reaction; less than a critical mass

supercritical mass | amount of material in which there is an increasing rate of fission

transmutation reaction | bombardment of one type of nuclei with other nuclei or neutrons

transuranium element | element with an atomic number greater than 92; these elements do not occur in nature

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18.10: Key Equations

$E = mc^2$

decay rate = λN

rem = RBE rad
Sv = RBE Gy

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18.11: Summary

An atomic nucleus consists of protons and neutrons, collectively called nucleons. Although protons repel each other, the nucleus is held tightly together by a short-range, but very strong, force called the strong nuclear force. A nucleus has less mass than the total mass of its constituent nucleons. This “missing” mass is the mass defect, which has been converted into the binding energy that holds the nucleus together according to Einstein’s mass-energy equivalence equation, $E = mc^2$. Of the many nuclides that exist, only a small number are stable. Nuclides with even numbers of protons or neutrons, or those with magic numbers of nucleons, are especially likely to be stable. These stable nuclides occupy a narrow band of stability on a graph of number of protons versus number of neutrons. The binding energy per nucleon is largest for the elements with mass numbers near 56; these are the most stable nuclei.

Nuclei can undergo reactions that change their number of protons, number of neutrons, or energy state. Many different particles can be involved in nuclear reactions. The most common are protons, neutrons, positrons (which are positively charged electrons), alpha (α) particles (which are high-energy helium nuclei), beta (β) particles (which are high-energy electrons), and gamma (γ) rays (which compose high-energy electromagnetic radiation). As with chemical reactions, nuclear reactions are always balanced. When a nuclear reaction occurs, the total mass (number) and the total charge remain unchanged.

Nuclei that have unstable n:p ratios undergo spontaneous radioactive decay. The most common types of radioactivity are α decay, β decay, γ emission, positron emission, and electron capture. Nuclear reactions also often involve γ rays, and some nuclei decay by electron capture. Each of these modes of decay leads to the formation of a new nucleus with a more stable n:p ratio. Some substances undergo radioactive decay series, proceeding through multiple decays before ending in a stable isotope. All nuclear decay processes follow first-order kinetics, and each radioisotope has its own characteristic half-life, the time that is required for half of its atoms to decay. Because of the large differences in stability among nuclides, there is a very wide range of half-lives of radioactive substances. Many of these substances have found useful applications in medical diagnosis and treatment, determining the age of archaeological and geological objects, and more.

It is possible to produce new atoms by bombarding other atoms with nuclei or high-speed particles. The products of these transmutation reactions can be stable or radioactive. A number of artificial elements, including technetium, astatine, and the transuranium elements, have been produced in this way.

Nuclear power as well as nuclear weapon detonations can be generated through fission (reactions in which a heavy nucleus is split into two or more lighter nuclei and several neutrons). Because the neutrons may induce additional fission reactions when they combine with other heavy nuclei, a chain reaction can result. Useful power is obtained if the fission process is carried out in a nuclear reactor. The conversion of light nuclei into heavier nuclei (fusion) also produces energy. At present, this energy has not been contained adequately and is too expensive to be feasible for commercial energy production.

Compounds known as radioactive tracers can be used to follow reactions, track the distribution of a substance, diagnose and treat medical conditions, and much more. Other radioactive substances are helpful for controlling pests, visualizing structures, providing fire warnings, and for many other applications. Hundreds of millions of nuclear medicine tests and procedures, using a wide variety of radioisotopes with relatively short half-lives, are performed every year in the US. Most of these radioisotopes have relatively short half-lives; some are short enough that the radioisotope must be made on-site at medical facilities. Radiation therapy uses high-energy radiation to kill cancer cells by damaging their DNA. The radiation used for this treatment may be delivered externally or internally.

We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources. This radiation can affect living organisms. Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes. Radiation can cause somatic or genetic damage, and is most harmful to rapidly reproducing cells. Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating but potentially most damaging and gamma rays the most penetrating.

Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure. We use several units to measure radiation: becquerels or curies for rates of radioactive decay; gray or rads for energy absorbed; and rems or sieverts for biological effects of radiation. Exposure to radiation can cause a wide range of health effects, from minor to severe, and including death. We can minimize the effects of radiation by shielding with dense materials such as lead, moving away from the source, and limiting time of exposure.

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